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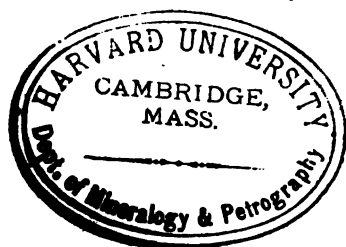
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AMERICAN JOURNAL OF SCIENCE

[FOURTH SERIES.]

ART. I.—*The Storm King Crossing of the Hudson River, by the New Catskill Aqueduct, of New York City*; by J. F. KEMP.

IN the Journal for October, 1908, there is a paper describing the buried channels of the Hudson and its tributaries in the portion of its course lying between New York City and the Catskills.* The paper was based upon data furnished by the exploratory borings of the Board of Water Supply of New York City, incident to the great Catskill Aqueduct which will soon be conducting the waters of Esopus Creek into the metropolis. At the time, the most interesting point of all could not be stated. It related to the bed-rock of the Hudson itself, where the Aqueduct was to cross, from Storm King Mountain on the west bank to Breakneck Mountain on the east. In 1908 we knew that with great difficulty the drill had been sent down in the middle of the river and that the hole was still in boulders and sand at a depth of 580 feet.

In the spring of 1909 drilling was resumed in the hope of reaching the bed-rock before the freezing of the river made further operations impossible for the season. The difficulties of casing and drilling these very deep holes, from an anchored scow, in water 40 to 60 ft., with a swift sweep of the tides, and with constantly passing traffic, are very great. The mixture of sand and boulders would be a serious obstacle even on land. With the greatest skill and energy on the part of the drillers the bottom of the hole at 768 ft. was still short of the bed-rock when the winter closed in. For reasons that will be next explained drilling from the scows was not resumed in the spring of 1910. This form of exploration therefore closed with the result of

* J. F. Kemp, Buried Channels beneath the Hudson and its tributaries, this Journal, xxvi, pp. 301-323, Oct., 1908.

the bore-holes with water and lowering to the ends of the holes a gage which would very accurately record the pressure of the overlying column of water, the progress of the holes could be plotted or checked in addition to the records of the cores. Horizontal variation was not measured. The horizontal component is more difficult to record than is the vertical and it was not considered necessary. As is well known to those familiar with diamond drilling, the holes are apt to swerve,

FIG. 2.

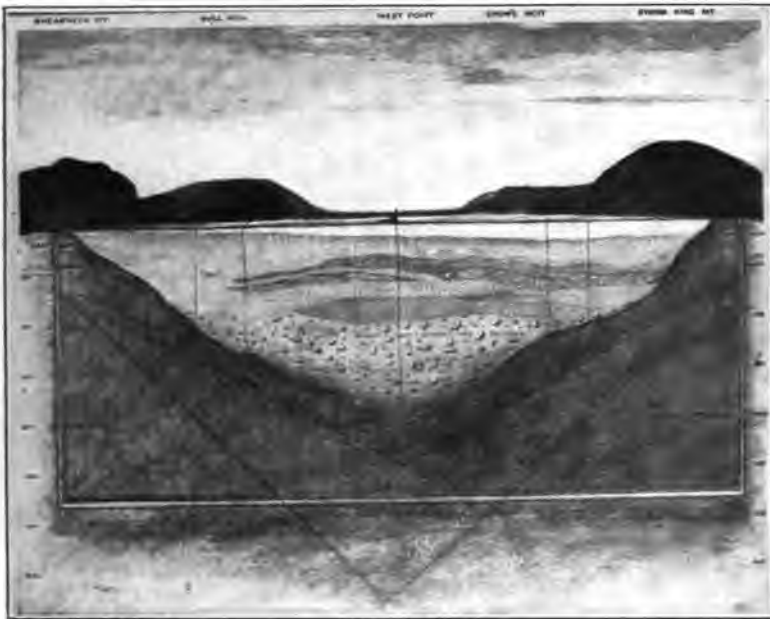


FIG. 2. Cross-section of the Storm King Crossing, plotted from the available data. The vertical scale is five-thirds the horizontal.

sometimes from encountering joints or surfaces from which the drill may cumulatively glance; or more seriously because of the tendency to turn upward from the sag of the long drill rods which do not fit tightly in the hole. The first pair of holes penetrated exceptionally firm and solid granite with occasional coarse diorite dikes until the depth gave reason to believe that the holes had crossed.

A second pair of holes were then started at such an angle that they would pass each other at approximately 900 ft. The drilling proceeded without incident worthy of remark, until the depth attained indicated that these holes also had

passed each other and that solid granite was present at the depth of 955 ft. A depth of 1100 ft. was therefore selected for the crossing of the great siphon; the shafts were pushed with all speed; the headings were turned and on Jan. 24, 1912, the last round of holes was fired, making the connection complete. The first man to pass through the tunnel from

FIG. 3.



FIG. 3. Topographic map showing the approaches of the aqueduct to the Storm King Crossing. Below and above the 400 contour, there is tunneling.

shore to shore, as soon as the powder-smoke had cleared away, was the Mayor of New York City.

The records afforded by the drills and the tunnel therefore demonstrated that the bed-rock of the Hudson lies somewhere between 768 ft. and 955 ft. below the surface. An estimate based on the profiles of the shallower holes nearer the shore and the assumed U-shaped profile of a glaciated valley, leads

to 800 ft. as a guess. More accurately than this it seems impossible to determine the depths with the data in hand.

Leaving in abeyance for the moment certain important conclusions which follow from this unexpectedly great depth, a few interesting features may be recorded regarding the tunnel itself. The greater portion of the rock is granite from shore to shore and for a mile or two on each side. It is a part of the large Storm King batholith which is so important a feature of this portion of the Highlands. Where fresh it is a pale green rock, moderately provided with dark silicates. It contains the usual quartz, orthoclase, and plagioclase, together with hornblende, less biotite and the accessories normally found in granite. It is obviously under compressive strain, since both in the shafts and in the tunnel the rock scales off, with small explosions, a process called "popping" by the workmen. In the shafts care became necessary to guard against injury from falling pieces. In the tunnel, where the popping tends to eat back into the roof and unduly enlarge the cross-section of the tunnel, lagging and arch-like supports of bent I-beams have been used to keep it from starting.

At intervals shown in the plan, fig. 4, the tunnel cuts at small angles the dark bands of diorite which were described from the cuts of the West Shore R. R. in 1888.* Eleven of these have been observed in the tunnel. They vary from a minimum of about a foot in thickness up to a maximum of 25 or 30 ft. The tunnel cuts them at such a slanting angle that it is difficult to make accurate estimates.† These apparent dikes are much richer in dark silicates than the granite and appear to be very old intrusive masses. They are thoroughly granitoid in texture, and consist of hornblende as the most abundant dark silicate, of pale, green monoclinic pyroxene, and rare biotite. The commonest feldspar is near labradorite, but orthoclase also appears, and quartz is not entirely lacking. The description of them as dikes is more likely to be true than to consider them as basic schlieren or segregations in the granite magma itself.

The granite is cut by well-developed series of joints: The master set runs at approximately the same course as the dikes, and is thus parallel to the great structural features of this portion of the Appalachians. The joints come into the tunnel at angles of 15 to 20 degrees with the course. There is another set nearly at right angles to the first. Still more rarely a set crosses the axis of the tunnel nearly at right angles with its

* J. F. Kemp, *The Dikes of the Hudson River Highlands*, Amer. Naturalist, Aug., 1888, 695-698.

† The bearing of the tunnel is N. 56° 35' 14" E. referred to the true north. The magnetic variation is 9° 40'. The dikes strike about fifteen to twenty degrees nearer north.

FIG. 4.

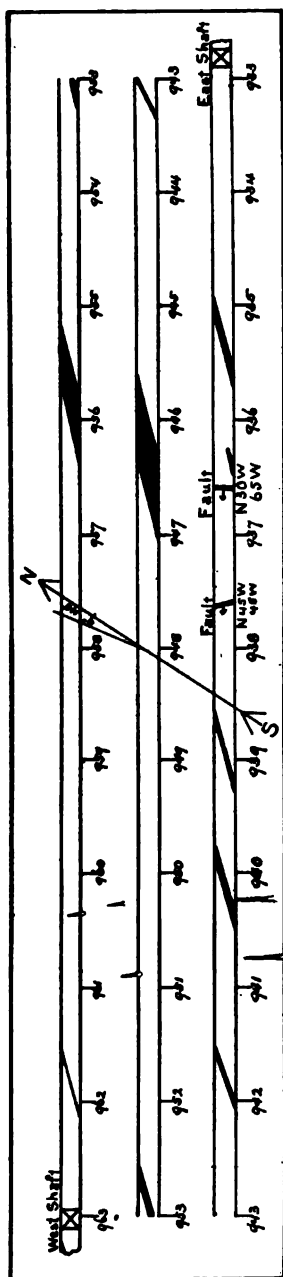


FIG. 4. Plan of the tunnel, 1100 ft. below the Hudson. The numbered stations are 100 ft. apart. The diagonal lines are the diorite dikes; otherwise the wall rock is granite.

course. In places the joints are more closely spaced than usual but nowhere to such a degree as to weaken the rock, more than is inevitable in large masses.

In the eastern half of the tunnel and respectively between Stations 936-937, and 937-938, two small faults have been encountered which are the chief and indeed almost the only source of water. The eastern one is the largest. It strikes about N. 30 W., almost exactly at right angles with the tunnel. It dips 65 W. There is no means of determining positively whether it is a normal fault or not, but it presumably is normal. The granite is crushed over a width of 2-3 ft. and is somewhat reddened by the oxidation of the iron-bearing minerals. There are slickensides coated with secondary silica. This fault is the most prolific single source of water in the tunnel, but the amount is nevertheless comparatively small. Its quantity and quality will be later referred to. If the fault is projected upward, it emerges in Breakneck Mountain, well inshore from the river's bank.

The second fault was encountered about one hundred feet west of the first and is much smaller. It strikes N. 45 W. and dips 45 W. There is only a foot or less of crushed granite but the slickensides are again developed and are coated with silica. A smaller amount of water is afforded. If this fault is also projected to the surface, it comes out in Breakneck Mountain. It is evident, therefore,

that despite the precipitous sides of Storm King and Breakneck Mountains no fault played any part in locating the river in its present course. On the contrary, it has cut its way downward into the granite without being directed by any plane of weakness. As has been suggested already by Dr. C. P. Berkey,* the river is doubtless a superimposed one and was probably guided at the outset by some soft overlying beds so that it became intrenched in the hard, crystallines. At a time of greater relative elevation of the land with regard to the sea, and presumably in the closing Tertiary period, as the Glacial epoch was approaching, the river cut its channel below the present surface of the Hudson and part of the way down to its present bed-rock. Reserving the further elaboration of this topic for a moment, it will be taken up again further on.

A very remarkable feature of the tunnel is the small amount of water which it yields. Although the tunnel is 3022 ft. from shaft to shaft, is 18 ft. in diameter, and traverses jointed rocks beneath the great river, the wall-rock is practically dry throughout much the largest part of its course. The west shaft and over 2000 ft. of the tunnel next it at present only yield to the pumps 30 gallons per minute. Much of this comes from the shaft itself and the larger part of the remainder from a jointed portion with an appreciable drip near station 960 (see fig. 4). At the time of the writer's visit, Feb. 6, 1912, a bench had been left at station 942 + 60, to confine the more abundant water from the faults to the eastern 1000 ft. of tunnel. At this date the east shaft and approximately 1000 ft. of tunnel draining into it yielded about 235 gallons per minute—a goodly part of which was derived from the shaft itself, near the upper pump chamber shown in fig. 2.

It is a very impressive experience to be lowered in the great shaft on the west bank to a depth 1100 ft. below sea-level, to walk for 2000 ft. through a tunnel 18 ft. in diameter beneath a great river and to observe wall-rocks which are practically dry except at one or two limited points. One may then continue another 1000 ft. and meet the same conditions except at the two small faults. The conclusion is greatly strengthened that the amount of ground-water in the rocks beneath the surface has been much exaggerated by the great majority of writers who have discussed the subject in the past.

The character of the water is also of much interest as compared with that of the Hudson overhead. Analyses show that the Hudson itself at the Storm King Crossing varies apparently at different stages of the tide. At the ebb with the

*C. P. Berkey, *Geology of the New York City (Catskill) Aqueduct*. Bull. 146, N. Y. State Museum, p. 95, 1911. Besides being a scientific record of observations of unusual accuracy, this Bulletin is an illustration of the applications of geological studies to a great engineering problem.

relatively larger proportion of fresh water its dissolved salts are generally less, but at the flood the sea-water brought up from New York Bay as a rule raises the percentages materially. The following table is from a series prepared in the chemical laboratory of the Board of Water Supply. They cover a period of four months in 1909. The chlorine is given in parts per million. It is believed to be combined with sodium in largest part, and in smaller part with potassium and magnesium. An analysis that is nearly complete follows the table for chlorine and calcium. It gives an idea of the relative proportions of NaCl, KCl, and MgCl₂. They are respectively 88, 2 and 10. The total chlorine should be divided in nearly the same ratios, viz. 87.6, 1.6, and 10.8. The calcium should be considered to be present as calcium sulphate.

Partial Analyses of Hudson River Water at Storm King.

1909		Cl	Ca	Tide
Sept.	1	1725.	18.5	Not recorded.
"	4	1068.	46.	
"	15	1475.		
"	22	1875.	57.	
"	29	2525.	92.	Flood.
Oct.	6	1575.	83.	Ebb.
"	13	2125.	96.	Flood.
"	20	1900.	82.	Ebb.
"	27	1900.	80.	Flood.
Nov.	10	2700.	98.	Flood.
"	17	2095.	96.	Quarter-flood.
Dec.	1	1825.	106.	Quarter-ebb.
"	8	2950.	158.	Quarter-ebb.

The results as a rule show more chlorine at flood than at ebb, but they are not uniform. The maximum value, the very last, is at quarter-ebb. The values give some idea of the ranges of the river water. Roughly calculated into NaCl, the chlorine should be increased one and one-half times.

On Sept. 11, 1909, the following analysis of the river water was made. It is expressed in parts per million.

NaCl	1940.
KCl	47.
MgCl ₂	212.
MgSO ₄	138.
CaSO ₄	156.
CaCO ₃	tr.
Organic	92.
Total	2585.

The following analyses, I and II in parts per million, were made of water which flowed from the granite through the inclined holes put down beneath the river. The hole is called $\frac{1}{A 74}$ in the official records. By the side of the two for comparison are placed three others, all expressed in parts per million. They are intended to show the contrasts of the deep waters with sea-water and the similarity to other deep waters.

	I	II	II	IV	V
	Bore hole beneath Hudson River	Bore hole beneath Hudson River	Sea- water	Quincy Mine, 47th level	Republic Mine, 1710' below surface
NaCl	5,231	6,607	28,119	29,600	18,510
KCl	294.	592
CaCl ₂	2,633.	2,013.	179,100	21,800
MgCl ₂	380.	277.	3,131
CaSO ₄	316.	354.	1,354	822
MgSO ₄	315.	248.	2,355	381
MgCO ₃	1,560
SiO ₂	8.
SiO ₂ and residue	113.	1,617
Al ₂ O ₃	700
Fe ₂ O ₃ , Al ₂ O ₃	7.	15.
Fe	4.
Cu	9.
Org. and vol.	926.
Total	9,816	9,808	35,664	208,713	45,390
“ Cl	5,125	5,619	19,660	132,500	25,360
“ Ca	1,049	816	398	64,500	7,904

I. Sample taken Aug. 27, 1909, from the deep bore hole, on the east bank.

II. Sample taken Sept. 11, 1909, from the same hole as No. I, but deeper down. On the same day the sample of Hudson River water was taken which is cited above.

III. Sea water analyzed by Forchhammer, as cited in J. Roth's Allg. und Chem. Geologie, I, 495

IV. Water from the 47th Level, Quincy Mine, Keweenaw Pt. Dr. G. A. König, analyst, cited by A. C. Lane, Lake Superior Mining Inst., June, 1908.

V. Water from the Republic Iron Mine, analyzed by G. Fernekes, cited by A. C. Lane as under IV.

If we refer back to the analysis of the Hudson River water and compare it with the samples from the bore holes, we see that the latter are much richer in chlorine, and that they are high in calcium chloride, which the river water lacks and

FIG. 5.

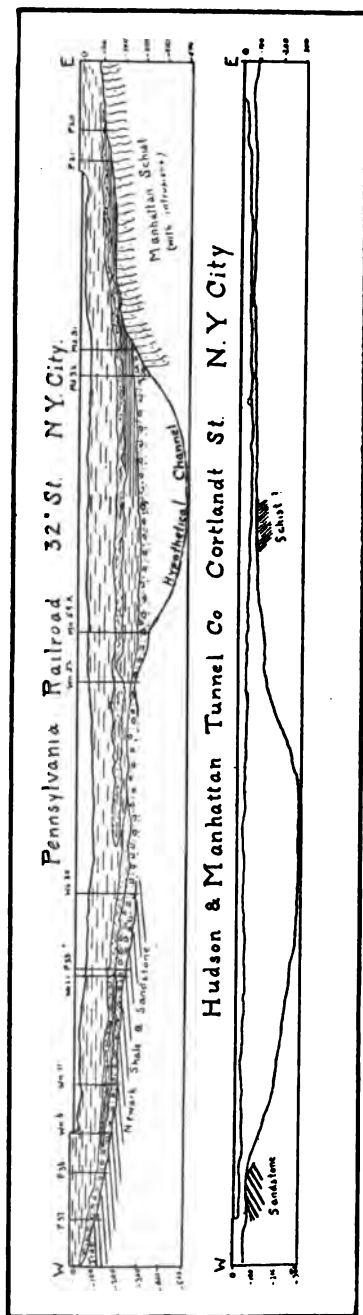


FIG. 5. Profile of the Hudson River opposite West 32d st., New York City, based upon data obtained by the Pennsylvania Railroad.

which also fails in the analysis of the sea water, No. III. On the other hand, in the two deep waters, Nos. IV and V, the calcium chloride is again high. The magnesium chloride, the calcium sulphate and the magnesium sulphate are all similar to the analysis of the sea water. Obviously the bore hole yielded a water which in its entirety cannot be referred to river or oceanic sources, although it may have an admixture of them. Its high calcium chloride is like the deep-seated waters of the rocks, which if ever derived from the surface, have undergone notable changes in chemical composition.

In the earlier paper, October, 1908, the writer in closing discussed the character of the lower Hudson Valley in the light of the depth as there determined for the bed-rock at Storm King. The deepest record was 608'6, but of course the middle of the river was then shrouded in mystery. It was assumed further that water was the sole eroding agent. No good data were available regarding bed-rock conditions from Storm King to the sea. The deep offshore channel of the Hudson had, however, been well developed by sounding.

Since then the data secured by the engineers of the Pennsylvania Railroad in connection with the tubes across the Hudson have been made available. A row of wash-borings has been put

down from the New York shore at West 32d street to New Jersey, and they have been supplemented by several diamond drill holes.* As shown by the accompanying cut (fig. 5), taken from Mr. Rogers' paper, the diamond drill borings are about 1100 ft. apart at the most important place and 900 ft. apart farther west. It is a very interesting question whether the bed-rock continues across these intervals at a depth of 300 ft., at which depth it appears on either side, or whether there is a deep and relatively narrow notch in the 1100 ft. stretch, so deep indeed as to permit water which had traversed the Storm King pass, 40 miles north at 800 ft. or thereabouts below tide, to reach the sea by a pass, necessarily still lower, opposite New York City. Advocates of water erosion as the cause of the Hudson gorge, would assume the existence of the notch. The bottom of the notch could not be less than between 500 and 600 feet below the nearest known bed-rock.

If water erosion is not the cause, then the Storm King pass has been over-deepened by some other agent than water. There is but one other agent and that is ice. Sub-glacial erosions would therefore follow. Opinion in America in recent years has been predominantly against glacial erosion, but various lines of evidence are making this process more and more probable. The Storm King Crossing would seem to be a favorable place for it.

Between Storm King and Breakneck Mountain the Hudson valley is very narrow, as is shown by fig. 3. A short distance north the old crystalline rocks end in a sharp fault escarpment which crosses the valley in a northeast direction. The softer Paleozoics have been easier marks for erosion than the hard crystallines and now present a broad valley. The same contrasts existed at the opening of the Glacial epoch. As the ice-sheet moved southward its only outlet was the narrow pass which was occupied by the river. The ice was crowded into this gorge and certainly was in as favorable a position to deepen its channel as ice under ordinary circumstances ever is placed. It may well be that in this way the channel was over-deepened and that as the ice-sheet approached the terminal moraine just below New York, it became gradually feebler and rose to higher levels, leaving in the end a shallower channel filled with ground moraine.

While not denying the possibility of water erosion with a notch at the Pennsylvania Railroad crossing, yet over-deepening by ice has been favored by Dr. Berkey and the writer in their reports as consulting geologists to the Board of Water Supply, but Professor W. O. Crosby, also reporting to the Board as consulting geologist, favors water erosion.

* G. S. Rogers. *The Character of the Hudson Gorge at New York City*, School of Mines Quarterly, xxxiii, 26-42, 1910.

ART. II.—*Lake Parinacochas and the Composition of its Water*; by GEORGE S. JAMIESON and HIRAM BINGHAM.

A SAMPLE of water from Lake Parinacochas was collected by one of us (H. B.) of the Yale Peruvian Expedition of 1911. The analysis of this sample is discussed in the present paper.

Lake Parinacochas is situated in Peru, between 15° and 16° S. latitude and 73° and 74° longitude, west of Greenwich. In other words, it is about 150 miles N.W. of Arequipa, and about 170 miles S.W. of Cuzco. Its elevation is about 11,500 feet above sea level. It is fed by half a dozen small streams or large brooks, and at present has no visible outlet. In past geological history it was much larger, and had an outlet which is still visible. In a river valley not many miles from the lake, and at a lower elevation, there are a considerable number of large springs which may possibly be fed by the lake. On the borders of the lake are also numerous small springs, which generally occur in swampy hillocks, three or four feet higher than the surrounding plain. The natives told us that in the wet season the lake was higher than in the dry season. The truth of this is evident from the marks of the salt left by evaporation of the lake as it shrinks during the dry season. In general the surrounding region is at present semi-arid, and is inhabited by a pastoral population. Thousands of sheep and some hundreds of cattle feed in the pastures which were formerly the bed of the lake. There are ruins of villages and agricultural terraces, indicating that at a previous period there was a much larger population here and that agriculture was more common than at present.

We spent eight days (Nov. 5–12, 1911) in three different camps on the shores of the lake and navigated it in a folding boat, the first boat or canoe that had been seen on the lake, according to the natives. We found that the lake was at present about 18 miles in length, and 7 miles in width, with a nearly uniform depth at the time of our visit, November, 1911, of 4½ feet. Several hundred soundings failed to show more than 5 feet anywhere. Judging by the salt marks on the shore, the lake is probably about a foot deeper in the rainy season. The natives told us that in the dry season the lake sometimes was very much lower than we saw it. The water has had a reputation of being brackish for nearly a century,—ever since any one took the trouble to say anything about it in print. The first and only reference to the character of the water that I have been able to find is in the *Memoirs of General William Miller* (London, 1828), where on a rough sketch-map he notes that the water of Lake Parinacochas is brackish.

FIG. 1.



FIG. 1. Lake Parinacochas, looking northeast. The extinct volcano Parinacocha shows on the right, the former outlet of the lake in the center, salt-covered shores in the foreground. The specimen of water whose analysis is published herewith was secured at the right-hand extremity of the lake. The panorama was taken by Mr. H. L. Tucker, archeological engineer of the expedition, from a hill partially covered with the ruins of a very ancient village.

Parinacochas is a contraction from the Quichua word "Parihuanakocha," which means *the lake of flamingoes*. The Quichua or Inca word for flamingoes is "Parihuana"; "Kocha" means lake. There are thousands of pink flamingoes, but we could find no evidence that they nested here. We found the lake to be the home of a great many birds, which, in the order of the frequency with which we saw them, are as follows: flamingoes, gulls, small divers, large black ducks, sandpipers, black ibis, large teal ducks, large geese, ground owls, and woodpeckers. Owing to the shallowness of the lake and the fact that a sweet marsh grass is abundant in

FIG. 2.

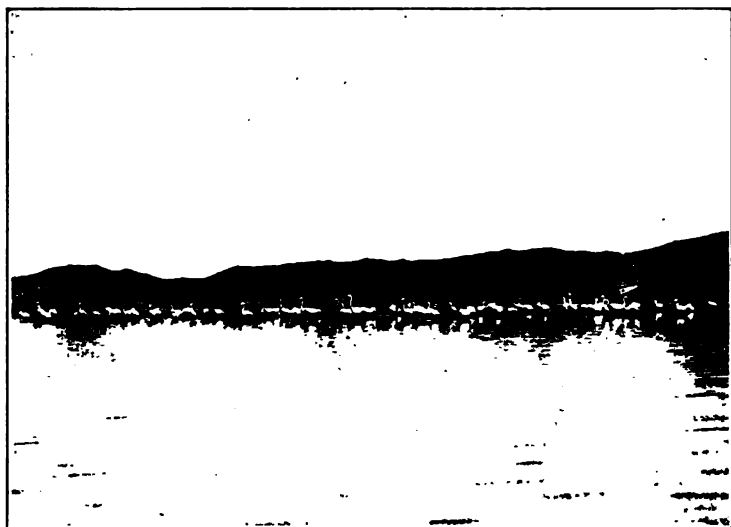


FIG. 2. Lake Parinacochas. Flamingoes wading in the lake.

it, the cattle are accustomed to wade sometimes as much as three quarters of a mile from shore, in order to get the particularly succulent grasses and water weeds. We saw no fish, and were told by the natives that there were no fishes in the water, but there was a great deal of small animal life. Large parts of the lake are covered with algæ, making it very difficult to row. In camps, near the banks of the lake, at night the temperature went as low as 22° F.

It will be seen at a glance, from the table, that the temperature of the water of the lake varies from 61° to 67·5°, depend-

ing chiefly on the time of day. In the mornings there is no wind, and the water near the surface is warmed by the sun. Shortly after noon a strong wind arises and stirs up the water and cools it near the surface, causing a slight fall in its temperature. The specimen of water was taken near the shore, in a location much frequented by birds and cattle.

Temperature of Water 10 in. below surface.

Water, near shore, 10:00 A. M., 61° F.

"	2½ ft. deep,	¼ mile from shore,	10:30 A. M.,	63·5° F.
"	3½ ft. "	¾ miles "	11:00 A. M.,	64° F.
"	16 in. "	150 yds. "	noon,	65·5° F.
"	3½ ft. "	½ mile "	12:30,	67·5° F.
"	4½ ft. "	1¼ miles "	1:00,	65° F.
"	4½ ft. "	1½ " "	1:30,	63° F.
"	4½ ft. "	1 mile "	2:00,	63·5° F.
"	4 ft. "	½ " "	2:30,	65° F.

The sample of water, which measured about 300°c, had a brackish taste and a slight brown color. The following results were obtained by analysis:

	Milligrams per liter.	Percentage com- position of the inorganic constituents.
Chlorine (Cl).....	5650·0	46·87%
Sulphate (SO ₄).....	1276·0	10·59
Carbonate (CO ₃).....	264·0	2·16
Borate (B ₂ O ₃).....	164·0	1·36
Nitrate (NO ₃).....	47·7	0·40
Phosphate (PO ₄).....	5·9	0·05
Silica (SiO ₂).....	8·0	0·07
Sodium (Na).....	3935·0	32·64
Potassium (K).....	464·0	3·83
Calcium (Ca).....	142·0	1·18
Magnesium (Mg).....	99·0	0·82
Iron (Fe).....	3·4	0·03
Salinity.....	12,059·0	100·00

The total residue obtained by evaporation at 100° C. was 12,548 milligrams per liter; the difference between the total residue and the salinity, amounting to 489·0 milligrams, represents in a measure the amount of organic matter held in solution. The following table gives the hypothetical combination of the acids and bases:

Sodium chloride.....	9324.0
Sodium sulphate.....	649.3
Sodium borate.....	212.4
Potassium sulphate.....	965.6
Potassium nitrate.....	78.0
Calcium sulphate.....	435.8
Calcium carbonate.....	33.8
Magnesium carbonate.....	342.8
Ferric phosphate.....	9.3
Silica.....	8.0

12,059.0

In order to compare the percentage composition of Lake Parinacochas with that of the Atlantic Ocean and several other typical saline waters, the following table is given. The analyses were taken from Bulletin No. 330 of the United States Geological Survey, entitled "The Data of Geochemistry," by F. W. Clarke, 1908 :

Water	Cl	SO ₄	CO ₃	PO ₄	B ₂ O ₃	Na	K	Ca	Mg	S ₂ O ₃	NO ₃	Fe	Total Salinity
1. Lake Parinacochas	46.86	10.59	2.14	0.05	1.36	32.63	3.85	1.18	0.82	0.07	0.40	0.03	12,059
2. Soda Lake, Nevada	36.51	10.36	13.78	----	0.25	36.63	2.01	trace	0.22	0.64	-----	-----	113,700
3. Atlantic Ocean....	55.48	7.69	0.21	----	----	80.60	1.10	1.20	3.72	----	----	----	34,400*
4. Great Salt Lake....	55.69	6.52	trace	----	trace	32.92	1.70	1.05	2.10	----	----	----	290,355
5. Lagoon of Tamun- tica, Chile.....	50.44	9.17	----	----	----	35.85	2.29	0.01	0.60	----	2.14	----	285,500
6. Koko Nor, Tibet...	40.05	17.84	5.53	0.02	----	30.60	1.08	1.77	2.90	0.09	----	----	11,000*

Analysts: 1, G. S. Jamieson; 2, T. M. Chatard; 3, G. Dittmaes; 4, E. Waller; 5, F. San Román; 6, C. Schmidt.

* An approximation only. Not given in the Bulletin.

On comparing the percentage composition of the several waters given in the table above, it is seen that Lake Parinacochas occupies an intermediate position. Its salinity is about one-third that of the Atlantic Ocean, or about one-twentieth that of the Great Salt Lake. It is also noticeable that it contains much more carbonate and much less magnesium than either the Atlantic or the Great Salt Lake.

Yale University, New Haven, Conn.,
April, 1912.

ART. III.—*On the Shell Heaps of Maine*; by F. B. LOOMIS
and D. B. YOUNG.

DURING the summer of 1909 a party of five from Amherst College spent two months working in the shell heaps of the Maine coast, one half of the time being devoted to a careful survey of one heap on Sawyer's Island, near Boothbay, the second month being spent in a more rapid investigation of several heaps for comparison.

These shell heaps are found all along the coast from Staten Island, Long Island, and the adjacent shore (there being some thirty of them in the neighborhood of New York City), scattering along the Connecticut and Massachusetts shores, and in ever increasing abundance along the coast of Maine, there being in that state a thousand or more in all, when big and little are counted. For over forty years some work has been done in them, mostly sporadic, and without real system; so that there are considerable collections in the Peabody Museum at Harvard, in the American Museum in New York, in the hands of Mr. Dwight Blaney on Ironbound Island, Maine, and belonging to Prof. J. T. Bowne of Springfield, Mass., not to mention a number of scattered collections. The abundance of the material and the widespread distribution of the heaps make it very desirable that systematic collecting and recording of the collections should be carried on. The vast number of the heaps indicate that they represent an important phase of the life of a large number of Prehistoric Indians.

The heaps vary greatly in size, from the one at Damariscotta, covering two or three acres, and some 20 feet thick, to tiny accumulations covering only a few square yards and only inches deep. In general, they are composed of the shells and refuse, which have been thrown away on a camp site, mixed with the ashes of camp- and cooking-fires, the bones of animals eaten, and bits of broken pottery, broken and lost tools, or anything which may be included in camp left-overs. The major part of the heap consists of more or less broken shells of the soft-shelled clam, though other mollusca may occur in great numbers; for instance, quahogs, blue mussels, or oysters, the great heap at Damariscotta being entirely composed of oysters: and there are usually bands in each heap composed entirely of other forms.

The heaps are located apparently with reference to camping convenience; nearness to drinking water, food supplies, and protection from storms, all being considered; so that near any big clam flat a shell heap may be looked for.

One finds the heaps in a variety of ways, the commonest being by observing the white gleam of the shells, where the sea has cut into and exposed the heap. Or they may be discovered as the result of plowing a field, whereby the shells are

FIG. 1.

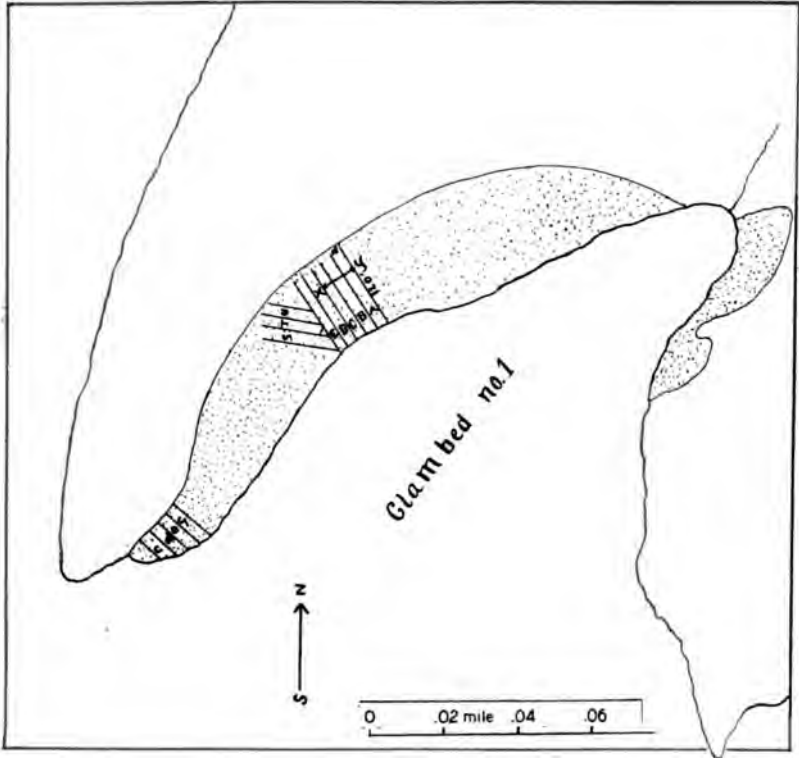


FIG. 1. Diagram of the south end of Sawyer's Island, showing the position of the shell heap, and the position and extent of the workings of the Amherst party. Scale, 1/1562.

brought to the surface; or by the bringing up of shells from rodent burrows, etc.

The Sawyer's Island heap was chosen for careful study, because it is of considerable size, and has never been disturbed by previous excavation, and also because it is located in a pasture, where the turning of it over caused very little damage. This heap lies on the southeast side of the island and in it two excavations were made, the first uncovering about 400 square

feet, where the depth of shells was about two feet; the second making a cut through the center of the heap, and covering over 2800 square feet, where the depth was about five feet.

The method used in working the heap was to plot out the surface in sections five feet wide, and as each section was worked, every find (of a tooth, tool, bit of pottery, etc.) was recorded, both as to its horizontal position and vertical depth. Everything with which man had anything to do was saved, except the shells and ashes. In this way the relative as well as the actual abundance of every article in the heaps was recorded.* Sections of the heap were plotted from time to time. The material from Sawyer's Island heap includes 1040 finds, each with an individual record, representing, of course, several times that number of bones. This material is the basis of the discussion of conditions on Sawyer's Island, and is supplemented by about three times as much from other heaps, where collections were made for comparison, and to give a basis for generalizations. Beside these, the collections above mentioned have been examined in order to make a check on any generalizations.

The character of any heap varies at different places and levels, but the following may be taken as a typical section :

No. 1. Sod with shells in the grass roots ..	3'
2. Shells with small amount of ash ...	14
3. Ashes with some shells	3
4. Clear shells	4
5. Ashes with some shells	4
6. Shells with small amount of ash ...	14
7. Clear ashes	6
Total earth	48 inches of shell heap.

No two sections are exactly alike, but everywhere there was the basal layer of ashes, and always the banded character of the material. In layers 2, 3, 5, and 6 the shells were very much broken up, apparently due to the tramping and building of fires on them. Where the shells were but little broken, and free from ashes, they would seem to indicate rapid accumulation, and offered but little in the line of finds. Under the heaps we found very few indications of the pits which are described as characteristic of the heaps along Long Island,† or

* In each case a recorded find indicates a tool, an animal eaten by the Indians, a pottery vessel, etc. Thus the record of an animal is based on the presence of a jaw, crushed fragments of bone, or single bones, though recorded, not being included in the enumerations. A score of fish vertebrae may indicate but a single individual, so in enumerating, the count is based on the number of premaxillæ. In the case of pottery fragments each assemblage of fragments is enumerated as one find.

† Alanson Skinner, American Museum Leaflet, No. 29, 1909.

those which are so characteristic of the Baum Village site in Ohio.* Only under the heap on White Island, and under the one on Calf Island, did anything of the sort occur, and neither of these pits was distinguished by having in it very much more

FIG. 2.

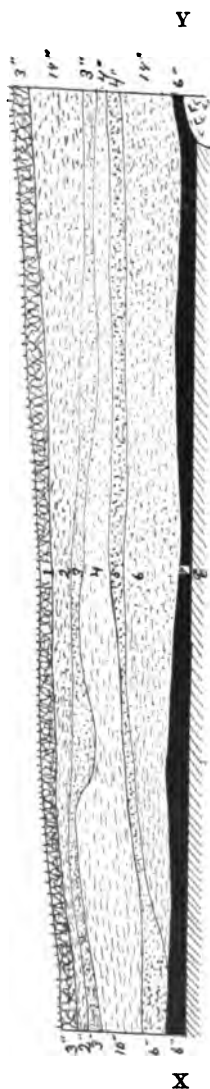


FIG. 2. Section of the Sawyer's Island heap, from x to y as on map fig. 1, showing the relative layerings of the shells, ashes, etc. Length, 16 feet.

than the neighboring portions of the heap. The bottom layer of pure ash would indicate that those camp sites were used for a long time before the habit of eating molluscs was acquired. Mingled in this layer were numerous bones, especially those of fishes, generally in the most disintegrated condition. The layer offered deer bones and all the other articles characteristic of the upper parts of the heaps. It will thus appear that *this and similar camp sites are older than the first shells, and it must be then deduced that the original object, of coming to the sea shore, was not clams but rather fishing, and possibly hunting, but especially fishing.* Where the layers were made of ashes and finely broken shells, the period of accumulation was longer and agreeing with that, the numbers of articles found in these layers was also greater.

Each of the heaps had its own characteristics, which can be seen by glancing down the columns of the lists of food-animals, and tools found. Thus Sawyer's Island is characterized by the tremendous abundance of deer remains, so that it would appear that the hunting must have rivalled the fishing, as doubtless this island was then a part of the mainland. The cod were also abundant and were doubtless the reason for the location of the heap. The heap on White Island differed from the others in that at the base of the heap was a considerable layer of oyster and quahog shells. On the north end of White Island there was a small heap almost exclusively composed of quahog shells.

The same was true of a heap on the north end of Birch

* Baum Village Site, Ohio Archæological and Historical Quarterly, vol. xv, pp. 1-95, 1906.

Island, but in neither case was there indication of long occupancy. The Flagg Island heap was at once distinguished by the presence of great numbers of large mink and of great auk bones and those of small fishes. It would seem as if these Indians were not the fishermen that those camped at Sawyer's Island were, for the remains of large fishes were very scarce, while those of flounders, cunners, etc., were abundant; but the apparently easily-caught, and staple food, on this Island was the great auk, the bones of which occurred in large num-

FIG. 3.

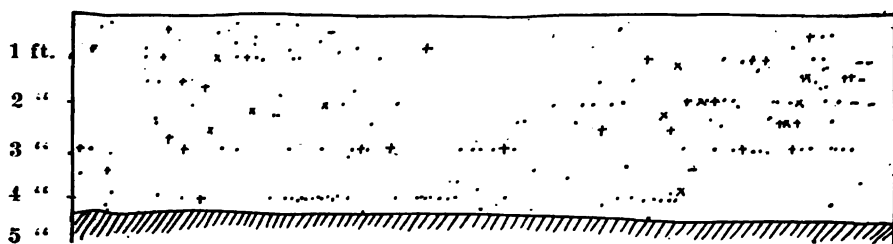


FIG. 3. Diagram of a section, fifteen feet long, along the line between B and C in fig. 1. All the material found in sections B and C is indicated in this figure, which therefore show the depth at which each find was made in these two sections and the relative abundance and relationship of the different articles. ● indicates a food animal, bone or jaw; + indicates a bone tool; x indicates a stone tool; — indicates bits of pottery.

bers, as did those also of many other birds, many of which we have not been able to identify. In Frenchman's Bay the heaps were dominantly of soft-shelled clams, but had in them frequent bands of blue mussel shells, a form occurring about the islands in vast numbers to-day. In these northern heaps moose bones become more abundant, and they are especially well characterized by the much greater proportion of stone implements found in them. The heap near Winter Harbor was perhaps the most prolific in bones and tools of any examined. It was distinguished by the quantities of cod and bird bones.

All these heaps, of course, represent camp sites, occupied for a longer or shorter period, by a smaller or larger group of Indians. Their fortunes varied annually, as is testified by the bones and shells left in the layers. It would seem that at first they did not come to get clams, nor did they even subsist on them. That was a secondary acquirement, but probably, when they began to use the shellfish, it became the staple food supply. The abundance of fish bones, the remains of fish hooks, and the broken harpoon points, indicate that the real business of the camp was fishing, and, presumably, the camp was timed to

catch the cod and haddock, when they came in near shore for the spring spawning, and were then in the greatest numbers and most easily caught. That they were spring camps is also confirmed by the condition of the horns on the crania of the male deer, which were found in the heap. In the Sawyer's Island heap, there were 54 male crania, of which only one had an attached horn. The time when the horns are entirely lacking is just after the shedding season, which is early spring, and coincides with the spawning time of the cod, etc. From these considerations, it seems almost a certainty that the camps were fishing camps, established in the spring, and only occupied by the Indian at that season of the year.

The heaps are found along the shore and on islands adjacent to the shore, often on very small islands, when there does not seem to have been available drinking water. Many or rather most of the heaps are being eaten into by the action of the tides and waves, so that in many cases what remains is only a fraction of the original area. This can only be explained by the fact that the land is gradually subsiding. On this point geologists are in general agreement, the outline of the coast being exactly that typical of a sinking coast line. It is further agreed that the coast, as far to the south as New Jersey, is also sinking, and the fundamental problem is the rate of subsidence. At New York City the rate has been determined, by a long set of observations of tide levels, as 1.64 feet per century.* In Maine the rate is probably somewhat more rapid, say three feet a century. Other evidences of sinking are found in the tide mills of early days, which are now so low as to be no longer available as power plants. Then there are numerous places where stumps and peat occur below tide level, the trees having been killed by the rising water. Lastly these heaps are also testimony to the sinking land, for the camps were beyond doubt originally well above the tide's reach.

In none of the heaps explored was any trace of iron implements found, showing that the heaps were completed before the advent of the whites, which began for trading purposes about 1627. The top of the heaps is therefore nearly three hundred years old, at least, and probably somewhat more. The length of time it took to accumulate the four or five feet of many of the heaps (more in some cases) can only be estimated, but as the camps were temporary, and the accumulation of ashes and broken up shells must have been comparatively slow, it would seem that not less than 300 to 500 years more should be added to the estimate for the age of the base of the heaps.

* This Journal, vol. xvii, p. 333, 1904.

Considering the age of the heaps, it must be concluded that the level at which the camp was originally established was some ten or more feet above the present level, and therefore many of the heaps now on islands, especially where these are near the shore, were then on the mainland.

Turning to the contents of the heaps, we may expect to learn from the contained articles many characteristics of the Indians who made the heaps. From the refuse bones, their food, and their hunting and fishing ability will appear; from the tools, their grade of culture, and something about their mechanical ability will also appear, while from comparisons with like rejects of other tribes, we shall learn something about their relationships.

The accompanying table gives all the sorts of food animals which we found and identified from the heaps. Some may not prove to have been food, but most were. Besides these there were a few species of molluscs, which occurred only once or twice, and were, therefore, simply accidental.

Deer (*Odocoileus virginianus borealis* (Miller) Allen) occur on Sawyer's Island in vast numbers, indicating that in this camp deer meat was a staple food supply. In other localities, their remains were comparatively infrequent, though always present. They were doubtless a highly prized food, and the remaining fragments of bones offer mute testimony to the Indian's pleasure in this meat, in the way every limb bone is split and crushed to get out the marrow, even such small bones as those of the toes being broken open, that none of the marrow should escape. Then the cannon bones, on account of their hardness, are a favorite material for making tools, likewise the antlers, when found. We found, however, no indication of the lower jaw being used for a tool, as was the case among the Indians of the Baum Village Site.* There were 53 crania preserved, of which 52 belonged to males, and only one to a female. Mills concludes, from a similar state of affairs in the Baum Village Site, that the Indians showed a foresight for perpetuating the deer in advance of that now exercised by man generally (loc. cit., p. 27). However, from studying the small fragments of other crania, we feel that the explanation is to be sought in another direction. The crania were always broken open to get out the brain. In the case of males with the heavy frontals, strengthened to support the antlers, the smashing of the brain case was done in the parietal region, the thickened frontals remaining intact: while in the case of females, the frontal bones being thin, the cranium was broken through this region, or they were at least also broken in getting the brain

* Ohio Arch. and Hist. Soc. Quart., vol. xv, p. 79, 1906.

**DISTRIBUTION OF ANIMAL REMAINS TO SHOW THEIR RELATIVE ABUNDANCE
IN THE VARIOUS HEAPS.**

The figures indicate the number of individuals found in each case.

	Sawyer's Island	White Island	North Harpwell	South Harpwell	Flagg Island	Calf Island	Seward Island	Winter Harbor
Deer (jaws)	703	3	2	1	2	2	3	--
Moose	2	--	--	--	--	--	1	5
Caribou	--	--	--	--	--	--	--	1
Dog, type 1	11	--	--	--	3	1	--	--
Dog, type 2	16	5	--	--	8	1	--	--
Dog, type 3	7	1	--	--	5	2	--	2
Fox	--	2	--	--	2	--	--	--
Wolf	5	--	--	--	--	--	--	--
Raccoon	6	1	--	--	--	--	--	3
Bear, black	3	2	--	--	7	--	--	--
Otter	4	1	--	1	1	--	1	--
Lynx	1	--	--	--	1	--	--	--
Mink ♂ sp. nov.	3	--	--	--	39	--	2	--
Mink ♀ "	--	--	--	--	14	--	--	--
Seal, harbor	3	2	--	--	4	1	1	1
Seal, Greenland	--	1	--	--	6	--	--	--
Whale	1	--	--	--	--	--	--	--
Beaver	20	2	3	--	8	6	--	5
Muskrat	--	--	--	--	1	--	1	1
Mouse, northern pine ..	5	--	--	--	--	--	--	--
Vole, meadow	2	--	--	--	2	--	--	--
Auk, great	1	7	4	--	50	3	5	8
Duck	--	--	--	--	1	--	--	--
Loon	1	--	3	--	3	1	1	--
Eagle	1	--	--	--	1	1	--	1
Goose	1	--	--	--	1	1	--	1
Birds, undetermined ..	5	5	10	--	45	7	8	27
Turtle	1	--	--	--	1	--	--	--
Frog	--	--	--	--	1	--	2	--
Cod	104	10	1	18	12	2	1	103
Haddock	11	2	--	2	--	--	--	19
Sculpin	--	1	--	--	9	--	--	3
Flounder	--	1	--	--	7	10	6	--
Cunner	--	--	--	--	32	--	1	--
Sturgeon	2	2	--	--	--	1	--	--
Dogfish	--	1	--	--	2	--	--	--
Clam, soft shelled	x	x	x	x	x	x	x	x
Clam, quahog	x	x	--	--	--	--	--	--
Helix	x	x	--	--	x	--	--	--
Mussel, blue	x	x	--	--	x	x	x	--
Oyster	--	x	--	--	--	--	--	--
Buccinum	x	x	x	x	x	x	x	x
Natica	x	x	--	x	x	x	x	x
Sea urchin	x	x	x	x	x	x	x	x
Total finds (shells omitted)	919	49	23	22	259	39	33	180

out. So only in males are the front parts of the cranium preserved intact.

Another interesting feature of the crania is the fact that 52 of the 53 crania belonged to individuals which had recently shed their antlers and had not as yet grown new ones. In other words, these deer were killed in the spring. The absence of individuals with partly developed or perfect antlers indicates, further, that the camps were simply spring camps, which also coincides with the best fishing season, and is the evidence that these heaps were made during periodic visits to the sites.

Moose (*Paralces americanus* (Clinton) Allen) is comparatively rare in the western and southern localities, but becomes increasingly abundant as one goes northward. As in the case of the deer, the limb and toe bones are split for marrow. This form would take the place of the deer in regions where it could be obtained. About half of the individuals found were young.

Caribou (*Rangifer caribou*, B. and A.) was only found once, and that in the Winter Harbor heap. It would seem that this form did not as a usual thing wander so far south as the Maine coast.

Dog.—Wherever Indian tribes have been investigated, some form of dog has usually been found, but as yet no one has made a systematic study of their remains. As with other tribes, these Maine Indians of the shell heaps had domestic dogs, of which our collection offers over 60 individuals. These are not more or less tamed wolves, but a very distinct type, having the shortened and concaved face characteristic of other domestic types. They are also much smaller than wolves, and range through three distinct types and sizes. The peculiar build and constant differences in size have led us to designate them as three breeds, which we believe date back a long period of time for their origin, and then from some of the wolves.

The largest breed (fig. 4B) is about a tenth smaller than the Esquimo dog of to-day, and may be designated as the *major Indian dog*, which is characterized first, by its size, the dental series of the lower jaw measuring 95 to 100^{mm} in length; second, by there being but 3/3 premolars, and last, by the plumper and heavier build of the teeth themselves.

The second-sized dog (fig. 9C), about as large as a shepherd dog of to-day, may be designated as the *common Indian dog*, and be distinguished by being of smaller size, the series of lower teeth measuring 87 to 91^{mm}, by having 4/4 premolars, and by the teeth being compressed from side to side and relatively smaller. This breed occurred most frequently, and it is of this sort that a nearly complete, though fragmentary, skeleton was found on Calf Island. The form is slender of limb and light

of build, like the shepherd dog, with which it compares in size also.

The smallest type (fig. 4D) or *minor Indian dog* is much smaller than the preceding, with a short heavy head, the lower series of teeth measuring 76 to 82^{mm} in length. There are as in the major type but $\frac{3}{3}$ premolars, and the individual teeth are plump, and closely set in a relatively short jaw.

FIG. 4.

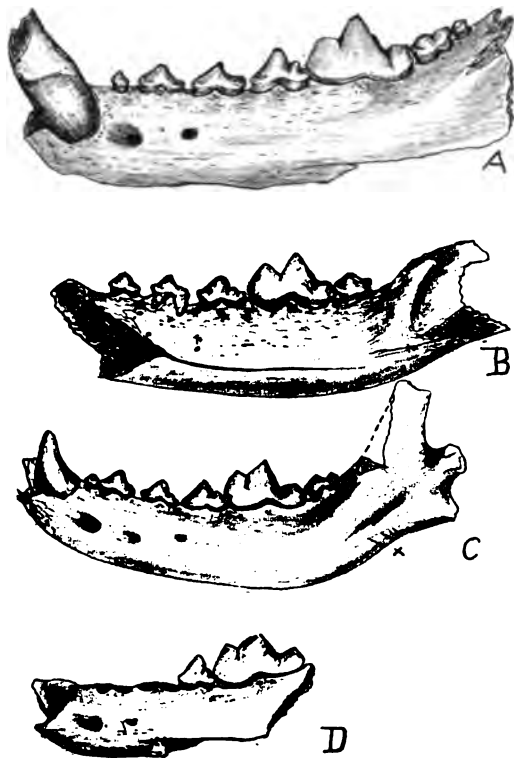


FIG. 4. Figures of the lower jaws of—A the wolf, B the major Indian dog, C the common Indian dog, and D the minor Indian dog; all $\frac{1}{2}$ natural size. The marks on the back of the common dog over x are tool marks.

Of the three types the last two are also present in the collections from the shell heaps of the vicinity of New York City, now displayed in the American Museum of Natural History. These two types are also found and are distinct in the collections from the cemeteries of Cross Co., Arkansas, now in the

Brooklyn Institute of Arts and Sciences. We feel that when a systematic study of the Indian dogs is made, it will be found that these three types have a much wider range than merely among the Indians of Maine. It is true that, as in the dogs of to-day, there are several jaws which do not fit exactly into any one of these groups, and they are presumably cross breeds, or grades of some sort, between the several types.

In two cases there are tool marks on the bones of the common Indian dog, and the dog bones are always scattered, in all but two cases, where burial had apparently taken place. This would indicate that the meat of the dog was commonly eaten. However, while the limb bones were generally broken they do not seem to have been split to get out the marrow, the eating of which seems to have been confined mostly to the deer and moose.

The *red fox* (*Vulpes fulvus* (Desmarest) Dekay) was very scarce, only four scattering jaws having been found. Evidently very little inland hunting and trapping was done.

The *timber wolf* (*Canis occidentalis* (Richardson) Baird) appears only in our collections from Sawyer's Island, and then not over five individuals are represented. It would seem that this locality was one where the best hunters were located, but even they did not care to go far for wolves. They may have been caught in traps.

The *black bear* (*Ursus americanus* Pallas) was turned up twelve times, which indicates a scattering representation. Again, it is an animal which was taken occasionally, when opportunity came to the campers, but was probably not systematically hunted. They were most abundant in the region of Flagg Island, which at that time was presumably a part of the mainland.

Of *raccoons* (*Procyon lotor* Stoops) only seven finds were made, so that the animal must be classed as an occasional article of diet.

The *otter* (*Lutra canadensis* Sabine) was another rare and only occasional find, being probably incidental in the make-up of the Indian food supply.

The *bay lynx* (*Lynx rufus* Rafinesque) was found twice, and would scarcely have been an animal easily caught by these early hunters.

A *mink** (*Lutreola macrodon*, D. W. Prentiss), different from any of the living species, was found occasionally in the various

* This species was first described by Prentiss, Proc. U. S. National Museum, vol. xxvi, 1903, p. 887. It was later again described by Loomis, this Journal, xxxi, 229, 1911, under the name *L. antiquus*, which should be considered as a synonym of the foregoing. See latter description for discussion of sex characters and relationships to other minks. This mink may have lived to historic times. See Forest and Stream, 1903, vol. lxi, p. 125.

heaps, but on Flagg Island the species occurred in such abundance as to represent a chief article of diet. The form is very large and heavily built, equaling in size the largest known minks from Alaska. During the week we collected on Flagg Island, 53 finds of this mink were made, which was a fifth of all the animal remains found. The males and females have the usual differences in size, the female being about 20 per cent smaller than the male. The locality about this camp must have been fairly overrun with these minks, and the campers have made a systematic business of trapping them. The whole heap was very different from most of the others in the character of the remains found, so much so that it seems as if fishing were here a subordinate industry to trapping and hunting.

Two seals inhabited the Maine coast in earlier times, the *Greenland seal* (*Phoca groelandica* Erxleben) and the smaller *harbor seal* (*Phoca vitulina* Linnaeus). Of these the former occurred very sparingly, the Maine coast probably representing the lowest part of its range. The harbor seal, though still abundant along the coast, and having been in known times an important item in the fisheries of the Indians, still seems in shell heap times to have been much less used, probably because it would have been rather difficult of capture with the primitive weapons of the period.

Parts of a *whale* (probably *Balaena glacialis* Bonnatirre) were found in the Sawyer's Island heap, and it must have represented a fortunate accident, when this great mass, of tons of meat, was stranded for the benefit of these Indians. Only a dozen chunks of the whale's bones were found in our excavation, which leads us to think that those present were brought to camp from some distance, where the whale was stranded, while other camps might well have also shared the find. All the bones are split, though there was no marrow to be obtained from them, but their large size made them peculiarly useful for making tools, and practically every piece is marked by the tools used in cutting and breaking up the whole bones. Two implements were found made of whalebone. The peculiar texture of whale's bones makes them adaptable to certain uses, and the stranding of a whale would have been of a rare enough occurrence to make it an occasion for utilizing all parts.

The *beaver* (*Castor canadensis* Kuhl) is a staple form found in all heaps, never in great abundance, but with great regularity. The remains occur either as jaws and limb bones or as isolated teeth, especially incisors. About half the individuals are young, and these seem to have been used only as a food supply. In the case of the adult individuals, they served the double purpose of a food, and material for making tools. The

incisors of the adult were very seldom found in the jaws, having been extracted to make cutting tools. On the other hand, in addition to the finds of beaver bones or teeth, there were 39 finds of incisor teeth which had been worked into tools. The beaver is strictly a fresh-water animal, and not particularly addicted to the coast, so the getting of these animals must have represented a systematic, and universal, skill in trapping. Occasionally bones were found which had been gnawed by beavers; so they must have come upon the shell heaps occasionally. This also indicates that they were abundant during the shell heap period, for while on a fishing expedition, the Indians would hardly make very great efforts to get beaver when they were abundant further inland.

The *muskrat* (*Fiber zibethicus* Cuvier) was occasionally found, three jaws having been turned up. It is only incidental as an article of food, and was probably taken when trapping for beaver or some similar form.

The *northern pine mouse* (*Microtus pinetorum scalopsoides* (A. & B.) Batchelder) was found once, when five individuals, all with complete skeletons, lay together in a little pocket. This can scarcely be interpreted as having anything to do with the Indians, but is rather a case where a nest of mice were killed by winter, or some other accident, and may have been contemporaneous with the building of the heaps, or later.

The meadow vole (*Microtus pennsylvanicus* Rhoads) in like manner occurred twice, each time two individuals with more or less complete skeletons, which could not be attributed to the Indians.

The *Great Auk* (*Plautus impennis* Linneus) was far and away the most abundant of the bird remains. While on Sawyer's Island deer was the staple article of food, on Flagg Island no other form occurs as often as the great auk. On Sawyer's there was but one find of the great auk made, but on the other sites it was always an appreciable element of the food supply.

Though on most of the sites it is evident that fishing was the chief business of the camp, on Flagg Island it would appear that it was catching birds, chiefly this great auk. Here cod remains were few, deer were scarce, but the auk and mink were abundant food articles. The character of this heap suggests that its inhabitants were experts in trapping, and the auk is a bird easily trapped or even captured with a club, or possibly bait.

Duck (*Anas boschas* Linneus) were unexpectedly scarce, being identified but once, and that on Flagg Island.

The *loon* (*Haliaetus leucocephalus* Linneus) too was found in small numbers in most of the heaps, and was probably sought rather for its feathers than for its meat.

The *goose* (*Branta canadensis* Linneus) occurred sparingly, being hard to capture. Some of these large birds were presumably caught while nesting.

In addition to the above, there were, especially on White Island, Flagg Island, and at Winter Harbor, considerable numbers of remains of small birds, which we have not been able to identify. So abundant were they on Flagg Island, that we conclude that the Indians, there, were adepts at catching birds, and used them for a very large portion of their food supply.

Among the reptiles, only two broken turtle shells (*Chrisemys*) were found, so it would seem as if they could hardly be considered as an element of the food supply.

Bones of frogs occurred three times, indicating that they were too scarce to form any regular part of the larder.

The *cod* (*Gadus callarias* Linneus) was the staple fish found in all the heaps, though in greatly varying quantities. The remains, when found as vertebræ, do not sufficiently represent the numbers in any locality, so that for purposes of counting the upper jaw (maxilla) is used, but in the lower layers of each heap these cranial bones are very much disintegrated, so that in the tables the numbers of fishes are invariably underestimated. However, Sawyer's Island caught cod in great numbers, though not nearly so many as Winter Harbor, for the work on Sawyer's Island covered four times as long as that at Winter Harbor. The scarcity on Flagg Island is very marked, and to be correlated with the abundance of auk and other birds.

The *haddock* (*Melanogrammus æglefinus* Linneus) were found where cod remains were found, but they occurred much more sparingly in the heaps than would be expected by the relative abundance of the two fishes in the sea to-day.

Sculpins (*Myoxocephalus octodecimspinosus* Mitchill) were probably caught only incidentally, but, having been caught, were brought to camp and eaten: for, presumably, these Indians, like the modern ones, utilized every animal for food, if there were anything edible about it. However, they would not have fished for such a form. On Flagg Island their remains are by no means scarce, and probably some were overlooked in digging, such tiny bones being hard to see.

The spotted flounder (*Lophopsetta maculata* Mitchill) made up an appreciable element in the diet of the campers on Flagg, Calf, and Seward Islands.

Cunners (*Tautoglabrus adspersus* Walbaum) were abundant on Flagg Island, but they did not occur in any of the other heaps examined, except one specimen on Seward Island.

The *sturgeon* (*Acipenser sturio* Linneus) was found occasionally, and was probably a great prize, the fishes being

of great size, one being enough to have fed a camp for a day. However as the fish do not occur in schools so far to the north, they must have been difficult to capture with the means at hand. Presumably they were caught in nets.

A few times the horny, first, rays of the dorsal fins of dog-fishes were found, but everything about the skeleton of a dog-fish is so perishable, and the form is so annoyingly abundant at the present time, that it is only fair to assume, that goodly numbers were caught by the shell heap Indians.

The *soft shelled clam* (*Mya arenaria* Linneus) was the dominant and characteristic shell of each heap, making usually the major part of the material from which heaps were built. The Damariscotta heap, however, is made entirely of oyster shells. There does not seem to have been any marked change in the shape or character of the soft shelled clam, from shell heap days to the present time. As noted on page 19 there was a layer of ashes under the shell heaps, evidence that the camps were originally for fishing and hunting. When other food was plenty, it is to be presumed that it was eaten, and that the clams were the reserve and sure supply, as they must have been, at times, the major portion of the supply, as seen, when a foot or more of solid shells was accumulated.

The *quahog*, or hard shelled clam (*Venus mercenaria* Linneus) was found in a few heaps, noticeably at the bottom of the heap on White Island, where they formed a layer of three or four inches, while on Birch Island there was a small heap about a foot thick made up of these shells. In this neighborhood the clams first eaten were of this species, later the soft shelled variety. This is further evidence that the heaps were developed more or less independently and derived their character very largely from the fauna of the locality.

Blue mussels (*Mytilus edulis* Linnens) occurred in most of the heaps in greater or less numbers, usually found as bands of much decayed shells. These shells did not seem to withstand the weathering as well as other kinds, so that they were usually found as layers of bluish powder. As these molluscs occurred in great masses, attached to the rocks below tide level, they must have always been available, and seem to have been used only when other food failed, so these bands were, or are, indications of times of famine. They occurred in great frequency in the heaps in Frenchman's Bay, which may be due to the greater vicissitudes of the weather there, or to the greater abundance of the molluscs.

Oysters (*Ostrea borealis* Lamarck) were found regularly near the bottom of the heap on White Island, along with the quahog shells. They make up the entire Damariscotta heap, having been piled up there in a mass 25 or more feet deep, and cover-

ing a couple of acres. In this case the shells belong to very large individuals, many of them a foot in length. On White Island the oysters form a layer only about three inches thick, and are relatively small. Evidently the occurrence of oyster shells accords with the former distribution of the species.

The large *whelk* (*Buccinum labradorens* Reeve) was found scatteringly in all the heaps, at all levels. Judging from the way they are brought up on the shore to-day by birds, and broken or left in the sun to die, that is probably what happened in the earlier days, and these do not represent food supplies but the incidental and natural occurrence of the form. In like manner *Natica heros* was found scattered in the heaps and for the same reason, they, too, being incidental and not a part of the food supply.

In some cases sea-urchins occurred, isolated among the shells, and then their presence is, as above, accidental; but in other cases there were in almost every heap bands, often two or three inches thick, of disintegrated sea-urchin shells. Such masses of fragments doubtless mean that in these cases the Indians used the urchins for food. Again, these look like cases when other food was scarce.

The consideration of the tools throws light upon the habits of the users, and supplements the points which have come out in the study of the food supplies. In most cases the animals which have furnished food have also offered material for the making of tools. The two studies supplement each other, and then the tools offer some further data as to the work done and the grade of development of the industries.

Following is a list of the various tools found, together with their relative distribution and abundance.

Beaver incisors were universally distributed and show work of various sorts, the front edge being sharpened, or reshaped to a narrower point by grinding away the sides. These are often further modified by the back being cut away or the dentine on the inner face being ground down, so that a much modified and important tool resulted. They were doubtless set in handles of bone or wood, and used for making grooves in wood and bone and for making pits and depressions in various materials. Beaver teeth like these were found in the Baum Village Site, and seem to occur in all Algonquin localities where bone tools are found. They are, however, very scarce in Iroquois localities. Until very recent times similarly worked beaver teeth were used by the Esquimos, both on the east and west coast. The bones of the beaver were not found worked at all.

Harpoon points were made mostly from the cannon bones of the deer, and vary from nicely finished single-barbed points up

	Sawyer's Island	North Harpawell	South Harpawell	White Island	Flagg Island	Calf Island	Seward Island	Winter Harbor	
BONE TOOLS.									
Worked beaver teeth.....	15	2	--	2	15	9	6	4	14 from Sawyer's are tips of deer antlers.
Harpoon points.....	9	1	1	2	6	--	2	5	
Fish-hooks.....	2	--	3	8	21	21	25	5	
Bone awls, simple.....	49	4	5	10	25	8	4	8	
Bone awls, double-ended..	4	--	1	--	3	--	--	--	
Awls made from the side toes of deer.....	7	--	--	--	1	--	--	--	
Blunt-pointed instruments	6	--	--	1	6	2	2	--	
Bone scrapers.....	9	--	--	--	--	--	--	2	
Netting needles.....	--	--	--	--	5	1	--	2	
Ornaments of bone.....	2	--	--	--	4	1	--	--	
Flaking tools.....	--	--	--	2	4	1	--	3	
Misc. worked but incom- plete tools.....	15	1	--	7	29	8	5	7	
STONE TOOLS.									
Blanks.....	8	--	1	--	5	4	3	2	Chips every- where.
Arrow heads.....	3	--	--	--	--	--	--	--	
Knives.....	19	--	1	--	1	--	3	--	
Celts.....	5	--	--	--	2	--	2	8	
Scrapers.....	--	--	--	--	6	--	4	--	
Hammer stones.....	20 ⁺	1	1	5	26 ⁺	3 ⁺	2	7 ⁺	
Pestles.....	2	--	--	--	1	--	--	1	
	175	9	13	39	160	58	58	54	

to much less skillfully made points with as many as seven barbs. In two cases the upper ends are finished off and a hole is made near the top, indicating that the point was used as a toggle, and fitted loosely to the end of a shaft so as to be detached in the flesh of the victim. These are indicative of an advanced skill in fishing. Many others show no indication that they were loosely attached, and seemed to have been fixed to the end of a shaft. These were probably used in spearing smaller fish.

The *fish-hooks* were all of the type in which a straight-pointed bone spike is set obliquely in the end of a small piece of pliant wood, and bound in place with a thong, such as were used by the Hudson Bay Esquimos. In some of the localities loose

points occur in great numbers, as on Flagg, Calf, and Seward Islands; while in other localities they are unexpectedly lacking, as on Sawyer's Island, where only two questionable hooks were found. Perhaps their fish were caught in nets. And also, as noted above, this camp was distinctively devoted to hunting deer. On the Winter Harbor site the remains of fish were most

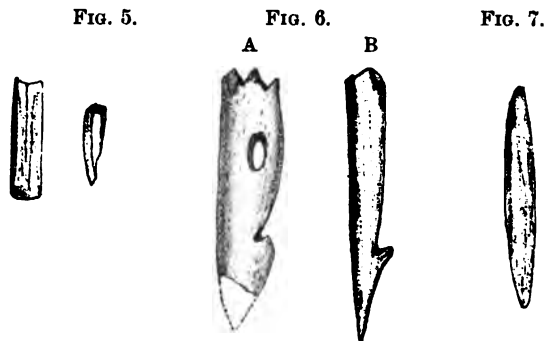


FIG. 5. Two beaver teeth, worked on the inner face and cut off at the back end.

FIG. 6. Harpoon points: A, arranged to be detached in the flesh; B, the type bound to end of a stick.

FIG. 7. A typical fishhook, $\frac{1}{2}$ natural size.

abundant, and here again the hooks were less abundant than in other localities, where other forms than fish were dominant. Our feeling is that these hooks were not the only, or even the typical, way of catching fishes. On Flagg Island the hooks were as abundant as in any locality, in spite of the great dearth of larger fishes, so that the hooks might have been used for the purpose of catching birds like the auk.

Bone *awls* were by far the commonest tools found. On Sawyer's Island they were mostly made of deer bones, on Flagg Island of dog and bird bones. The awl varies all the way from the carefully shaped and polished two-ended tool to rough splinters, on which one end is ground to a point. The carefully made double-pointed awl was doubtless a domestic implement of considerable value, and probably used for perforating the skins, for sewing them together, as is done by the modern worker in leather even to-day. The larger and heavier awls, made from the tips of antlers, the ulna of the dog, etc. were used on the larger and heavier skins, while the finer work, as on moccasins and clothing, was done with the smaller and slenderer tools, such as those made from bird bones, the side toes of deer, or the ulna of the mink. Some of the finest of these points show the most careful workmanship. In

cases where the hollow bones of birds were used to make awls, the upper end was usually left on for a handle and to strengthen the tool. Beside these awls there were a large number of rough splinters, sharpened to a more or less slender point, but with very little work or finish. These would be adapted to serve only as forks, for taking bits of hot meat from the pot, etc., their rough edges unfitting them for sewing or for long continued use. They were apparently quickly made, carelessly used, and often lost and broken.

FIG. 8.

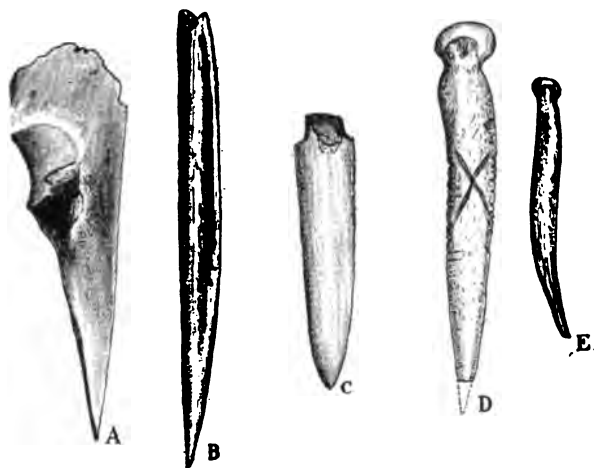


FIG. 8. Awls of the heavier types: A, made from the ulna of a deer; B, pointed at one end, notched at the other; C, very carefully made; D, from the side toe of a moose, and ornamented; E, from the side toe of the deer. $1\frac{1}{2}$ natural size.

Then there were a number of instruments with blunt ends, so that they were not adapted as perforating tools—but carefully made and skillfully finished; hence, while we have not been able to assign to them their uses, they were doubtless implements made for specific uses about the camp.

A few *needles*, consisting of cut pieces of ribs and from three to eight inches long, perforated in the middle, and rounded at either end, were doubtless used for making nets, as they are similar to netting needles used down to recent times. They are the only direct indications we have of nets, but they probably had nets just as they did when first known to the whites.

Bone *scrapers*, or *beaming tools*, were made from the cannon bone of the deer, the middle being cut partly away, and the

edges of the opening thus made being ground sharp. Such beaming tools have been found as far south as Long Island, and were abundant in the Baum Village Site. In our heaps, these tools vary considerably, the largest being made from the cannon bone of the moose, while others were made by cutting a deer antler lengthwise, its curves making it doubly effective. Some were even made from pieces of whale bones. They were used in removing the hair and flesh from hides in the process of making rawhide, etc. A hide laid over a log could be worked

FIG. 9.

FIG. 10.

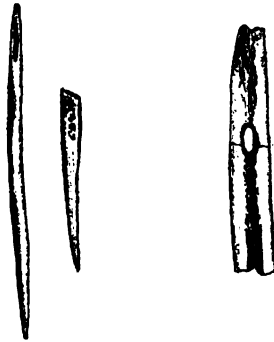


FIG. 9. Two types of needles. 1/2 natural size.

FIG. 10. Netting needle. 1/2 natural size.

with these tools much more effectively than when hung, not to mention the greater ease in doing the work.

Flaking tools were not rare, consisting of squared pieces of bones, cut from the solid parts of heavy bones, or from antlers, and varying in size from two to five inches long.

Bone was also sometimes used for *ornaments*, for instance a comb simply ornamented and having five teeth which had been broken before it was discarded. No teeth perforated to be hung on the neck were found, though one, with a groove around the root, did turn up. One small bar of bone, with a series of pits on either side, appears to be a counting stick in some game. Other odd and isolated finds occurred, not to mention the considerable quantity of unfinished implements, which were either broken in the manufacture or discarded because unsatisfactory.

One article is striking by its absence throughout all the heaps investigated, and that is the bone arrow point, which occurs in the burials on Long Island and in the adjacent refuse pits, both made apparently by the same people as those on the Maine coast. Then in the Baum Village Site the bone arrow

point is the most characteristic feature. Presumably the absence is to be accounted for by the fact that the Maine Indians used stone arrow points.

The stone implements were those usual to the regions of the interior of Maine and Massachusetts, wherever Algonquin tribes are found. Arrow heads, knives of various patterns, celts, scrapers, pestles, and hammer-stones, were all of familiar types, but it is noticeable that the farther to the north collections were made, the greater the relative abundance of the stone tools. Everywhere the rounded beach stones of con-

FIG. 11.

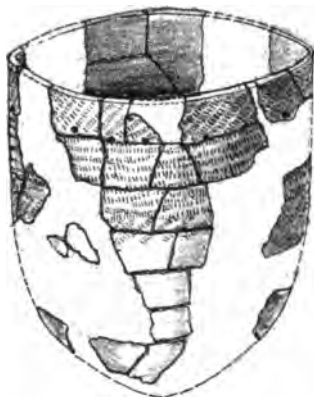


FIG. 11. Pot found on White Island and restored, showing form and ornamentation. $\frac{1}{4}$ natural size.

venient size were used as hammers. Many of them show only a small amount of wear, and as they were convenient to the hand they were probably used without a handle, for breaking bones, etc. Such are little worn. Others show the much bruised end which indicates that they were extensively used, and always on the same end, and that they were attached to a handle. Lastly there are a number which were carefully formed from flint, having been chipped down to their present form. These again had been long used and carried far.

Besides the above there were everywhere abundant stones which were cracked and disintegrated by the heat of fires, and were doubtless the fire stones placed about their camp fires, and used in cooking.

Fragments of *pottery* were found in all the heaps, though never abundantly; hence they seemed to represent the remnants of storage and water vessels. In two cases enough of a pot was found so that it could be reconstructed, in part

at least, enough to show size, shape, and ornamentation. Generally the most bits of pottery were found in the lower parts of the heaps, especially in the layer of ashes, which is doubtless due to the fact that it took longer to accumulate that layer.

The material used in the manufacture of the pots is clay, mixed with two sorts of tempering material, the tempering being introduced to overcome tendencies to shrink unevenly, and to crack in the firing process. In a majority of the vessels the temper was given by adding coarsely powdered rock, for the fragments found show quantities of particles of quartz, feldspar, and especially the scaly flakes of schist. Some of the particles are an eighth of an inch in diameter, while in other bits of pottery they are much finer. The dominant rocks in Maine are schists with veins of quartz, with any amount of granite boulders on the surface. This would seem to be the material ready at hand. In other cases the temper is entirely powdered shells, and this pottery is the tougher and better preserved. The two sorts of tempering material were not mixed in any of our finds. We surmise that the pots made while the Indians were in the interior were tempered with the powdered rock, while those made at the sea shore were tempered with the powdered shells.

In the two cases where enough fragments belonging to a single pot were found, so that it could be restored in part, the pots were of the tall round-bottomed type, characteristic of the New England Aigonquins, and none of the fragments would indicate a pot of any other form. Inasmuch as the fragments of the bottoms of pots were not more burned than the top pieces, it would appear that they were not used for cooking, but rather as containers of corn, liquids, etc. One of the most complete was found in the heap on White Island, two-thirds of the rim being present, and also one side down to the base. This was six and a half inches across the top and seven and a half inches high. The second good pot was found in the Sawyer's Island heap, had over half of the rim, and measures nine and three-quarters inches across the top, being apparently not quite so deep. Such pots could not stand on their bottoms and must have been set in baskets or hung up; but there is not any indication of their having been hung up, unless it is a row of holes was made just under the rim and about an inch apart. Each hole goes about three-quarters of the way through the rim, but none clear through. They were undoubtedly used in some manner for a grip, and may have been connected with some method of hanging the pot, but seem to us to be rather for handling the pot while being baked.

The edges of the fragments of these two pots, and in many of the other cases also, show that the pots were made by taking

flat strips of clay (each about an inch wide in case of the White Island pot) and building up the pot, by making first one tier, then by rubbing to make the two adhere, then another layer and so on. In the Southwest pots are frequently built up by taking a long and narrow strip and winding them around and building up spirally until the pot is formed, but in this case there is no trace of the spiral structure, only a very clear evidence of one ring of clay after another. After the

FIG. 12.



FIG. 13.

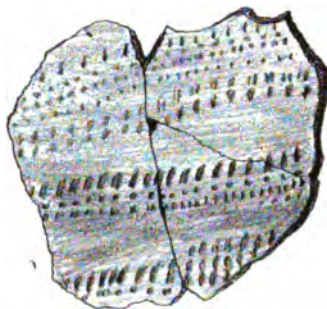


FIG. 14.

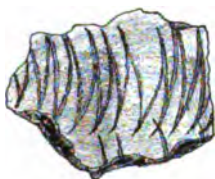


FIG. 12.—Fragment of the rim of a pot showing ornamentation by use of the simple end of a stick. $1/2$ natural size.

FIG. 13.—Fragment of pottery with pattern resulting from use of more complicated tools, and the use of more than one tool. $1/2$ natural size.

FIG. 14.—Pattern resulting from the use of a rotated disc on a handle. $1/2$ natural size.

pot had been roughly built up it was smoothed down and carefully shaped, the surface being prepared for whatever ornamentation it was to receive.

On the pots from the Maine shell heaps the *ornamentation* was of the simplest, there being no trace of coloring, and the patterns being imprinted on the surface. None of the pots had any incised pattern, in which they are very distinctive and also primitive. There were but few methods of impressing the ornamentation, the simplest being by using the end of a stick which had been squared or rounded in various shapes, a series of similar indentations being put on the pot as in fig. 12. A modification of this is seen when the stick was cut into a paddle form and along the edge a series of notches or teeth was made. The White Island pot is decorated with such a comb-like stick, the rim being covered with a series of these impressions put on

obliquely; then below this a broad belt of the same indentations put on horizontally to make a banded effect; and finally a lower band where the same figure is again faintly impressed obliquely. The Sawyer's Island pot was decorated in the same manner, the teeth of the comb-like tool being coarser, and in this case the rim has a vertical series, then a broad band put on horizontally, and finally below another series of vertical impressions. In some cases the end of the paddle or comb was notched or cut into teeth of irregular size, so that a more varied pattern resulted, and the most elaborate fragments have a pattern made by using more than one tool. See fig. 13. In a very few cases a disc attached to a handle* was used, which is

FIG. 15.



FIG. 16.



FIG. 15.—Pottery object of unknown use, but incised. Unique in the heaps. 1/2 natural size.

FIG. 16.—Stem of an ornamentated pipe found on Sawyer's Island. 1/2 natural size.

a more highly developed manner of decoration. When the disc was rotated back and forth on the clay, such a pattern as that in fig. 14 resulted. If the rim of the disc was notched the pattern was correspondingly more elaborate. This manner of working was, however, very rare, not occurring more than three times in over fifty finds.

The only case of an incised pattern was on a single bit of baked clay, not formed to any discovered use, and which may have been a whim or an ornament. Fig. 15 shows the find, and we feel that it was brought into the region, having been made elsewhere. Except for this, incised work is entirely lacking. The patterns made with the more or less worked stick are characteristic of the Algonquins, not only of this district but also on the Atlantic coast further to the south and in the middle west. Incised pottery is characteristic of the Iroquois and their influence is felt in the pottery of the adjacent tribes as is seen in the usual pottery found in Massachusetts and Connecticut, but the Shell-heap Indians do not seem to have been influenced in the least by the Iroquois. It is true that the work of the Maine Indians is of the crudest grade of impressed ornamentation, and suggests that these

* For methods of putting on ornamentation see Holmes, *Aboriginal Pottery of Eastern United States*, 20th Ann. Report Bureau of Emer. Ethnology, 1899, p. 76.

people had not attained the grade of advancement shown by the Algonquins in other sections.

Pipes, which so generally form an interesting part of the finds in Indian refuse heaps, were very scarce, only two being found, both broken, but both made of the shell-tempered clay. They are of the thick flaring type with a very clumsy stem and apparently a small bowl, which was either a widening of the distal end, or was curved slightly upward. There is nothing about them to suggest Iroquois.

The group of Indians which built the shell heaps would, from the foregoing, seem without question to have been Algonquins, and show many characters relating them to the middle west members of that great tribe; but in the lack of bone arrow heads, in the absence of the curved fish-hook, in the scarcity and great simplicity of the pottery, they are much less developed than the Ohio and neighboring tribes. They are separated by the great Iroquois nation and had probably been isolated for many generations, and preserved the more ancient and primitive culture. The Abnakis living there, when the state was first settled by whites, were doubtless a remnant of the former shell-heap-building Indians.

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Amherst College.

ART. IV.—*Mixtures of Amorphous Sulphur and Selenium as Immersion Media for the Determination of High Refractive Indices with the Microscope*; by H. E. MERWIN and E. S. LARSEN.

THE difficulty of identifying transparent minerals and other solids the refractive indices of which can not at present be determined under the microscope because of the lack of suitable immersion media, has led to the following experimental studies.

In a molten condition sulphur and selenium are miscible in all proportions. The mixtures can be melted readily on a glass slip held over a low flame, and when melted readily adhere to pulverized minerals. The cooled mixtures rich in selenium remain amorphous for months, those very rich in sulphur may crystallize almost immediately on cooling or after some hours or days, according to the conditions of heating and cooling. With increasing selenium the refractive indices of the mixtures increase from about 1.98 to 2.92 for sodium light and from 1.96 to 2.72 for lithium light.

The mixtures containing less than 50 per cent Se by weight, if heated on a glass slip to near boiling and then cooled in air, crystallize more slowly and have slightly higher ($\cdot 010$) indices of refraction than those which, after having crystallized, are barely melted and similarly cooled.* This is probably due to the presence of varying amounts of the two allotropic forms of molten sulphur. With increasing Se these effects of differences in heating and cooling diminish.

Having given the refractive indices of such mixtures for light of various wave-lengths (Chart I) it only remains to match

* By quenching some of the highly heated mixtures in water, the refractive index has been raised $\cdot 05$ above the values obtained by cooling in air.

the refractive index of the substance under investigation with the refractive index of a mixture by one of the well-known microscopic methods.* The matching can be done as closely as ± 0.01 in monochromatic light. It is, then, the variation in the refractive index of the mixture that limits the accuracy to ± 0.005 . It is possible to exceed this accuracy by taking account of the conditions as later described, but it is only in exceptional cases that great accuracy is desired. A series of mixtures suitable for approximate determination is given in Table I.

If the observations are made in white light the dispersion and color of the mixtures introduce other factors of error.

TABLE I.

% Se	n_{Li}	n_{Na}	Equivalent wave-length $\mu\mu$	% Se	n_{Li}	n_{Na}	Equivalent wave-length $\mu\mu$
0.0	1.978	1.998	---	57.0	2.200	2.248	620
9.0	2.000	2.022	---	64.0	2.250	2.307	630
17.6	2.025	2.050	---	70.0	2.300	2.365	633
25.0	2.050	2.078	---	75.0	2.350	2.423	636
31.8	2.075	2.107	---	80.0	2.400	2.490	640
37.5	2.100	2.134	---	87.7	2.500	2.624	645
43.2	2.125	2.163	580	93.8	2.600	2.755	652
48.2	2.150	2.193	605	99.2	2.700	2.90	662
53.0	2.175	2.220	615	100.0	2.716	2.92	665

The mixtures containing less than 45 per cent Se are yellow or orange. The other mixtures have a deeper red color, and their refractive indices must be expressed in certain wave-lengths of red light. The simplest and best way is to observe the preparation through a thin film of Se pressed out under a cover-glass on a glass slide, and used as a screen over the eyepiece of the microscope. Such a film transmits light which is almost equivalent to Li-light.† This screen may be used with any of the mixtures for determining approximate refractive indices for Li-light. The intensity of the light through this screen, if the source of the light is the sky, is low but sufficient for ordinary work, though an artificial light—an

* See F. E. Wright, *The Methods of Petrographic-Microscopic Research*, pp. 83-98, 1911.

† The film of Se transmits a narrow band of the spectrum in the red, of which the chief intensity lies between wave-lengths 650 $\mu\mu$ and 680 $\mu\mu$. This is equivalent to wave-length 665 $\mu\mu$. The wave-length of Li-light is 671 $\mu\mu$.

incandescent electric, for example—is preferable. The wave-lengths to which artificial light transmitted by thin films— $\cdot 05$ to $\cdot 10$ thick—of several of the mixtures is approximately equivalent are given in the table.

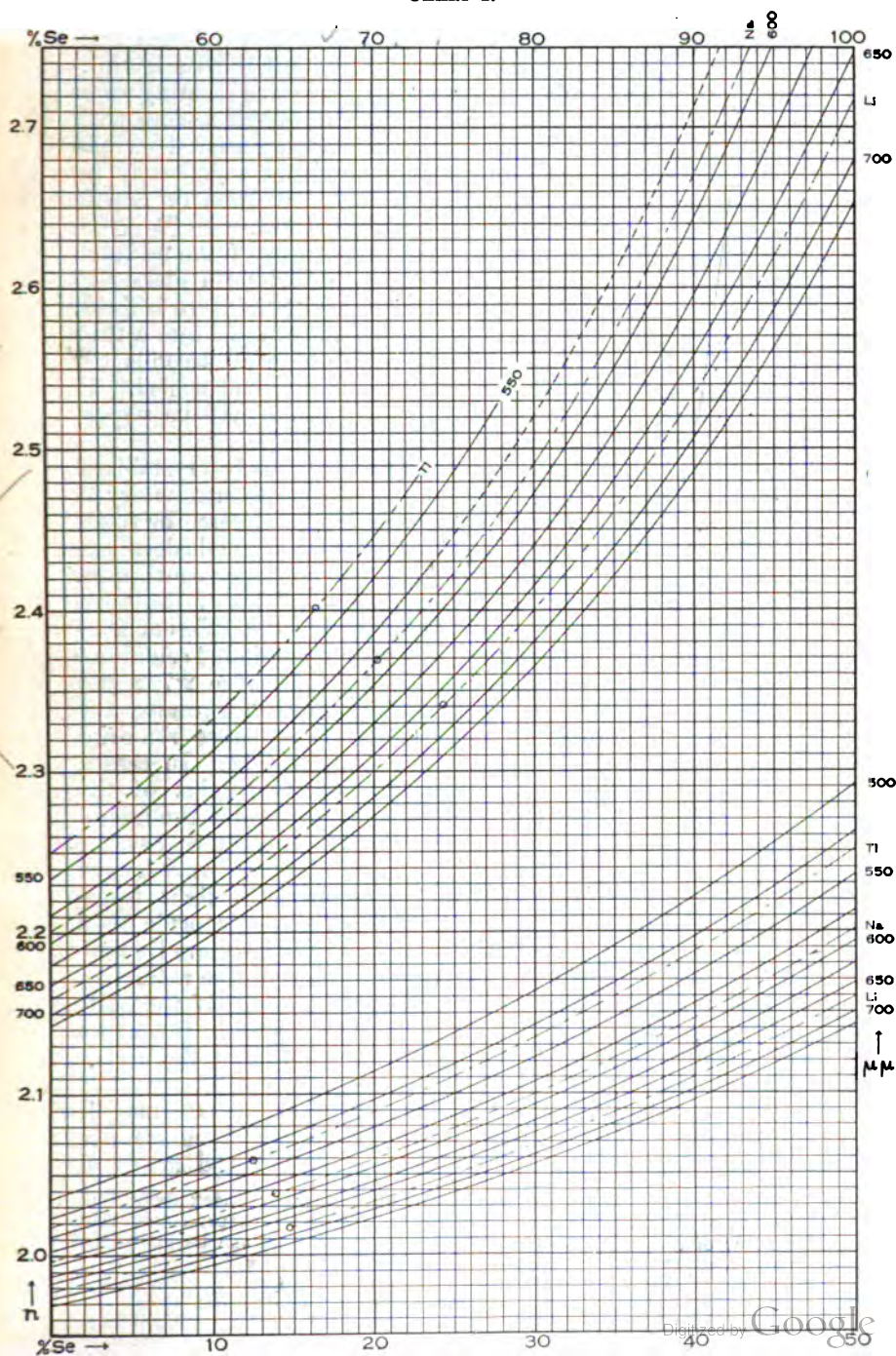
The material under examination should be finely powdered so that the mixture may be pressed out into a thin film. If the material is colorless and no screen is used the excess of white light passing through it may obscure the light-and-shadow effects at the boundaries of the larger grains. Smaller grains that are more deeply covered by the mixture should be observed.

If it is desired to obtain results with errors as small as $\pm \cdot 005$ it is essential to use monochromatic light or suitable screens, owing to the extremely high dispersion of Se. For Se the two Na lines have a difference of refraction of $\cdot 004$. Two lines having the same difference of wave-length near the Li line have a difference of refraction of $\cdot 0013$. Lithium light can be used with all the mixtures. If it is contaminated by sodium light the sodium light may be filtered out by using the screen of Se above described; or a film of celluloid or gelatin stained with methyl violet may be used. The Na-flame can not be used with mixtures containing more than about 70 per cent Se.

A spectroscopic monochromatic illuminator may be used to advantage, particularly as a time-saver. With it the necessity for making up a mixture which exactly matches the refractive index of the substance studied for a particular wave-length is obviated. An approximate match may be made in white light, then with the same mixture the wave-length at which the refractive indices are alike can be found by means of the illuminator. As most transparent solids have very much less dispersion than the mixtures, another mixture can now be selected which will match the refractive index of the substance for a very different wave-length. Then the refractive index of the substance for one or more of the commonly used standard wave-lengths (*Li*, *Na*, *Tl*) can be obtained without great error by interpolating along a straight line drawn on the chart between the two points representing the observed refractive indices.*

* All the available high refractive indices of minerals of known dispersion have been tested by plotting on the chart. Those for which interpolation gives the greatest errors are sphalerite and sulphur (β). The refractive indices of these minerals for certain wave-lengths are represented on the chart. The slopes of lines through any given point indicate the relative dispersion of the substances which the lines represent. For example, the slope of the line for sphalerite is about 45° ; if it were 60° , the dispersion would be greater; if 90° , the dispersion would be still greater and equal to that of the mixture. For most minerals the slope is about 45° . It is obvious that after having obtained and plotted a first value of the refractive index for a chance wave-length, a line through the point with a slope of about 45° will indicate approximately the mixture to use in finding the refractive index for any desired wave-length.

CHART I.



The mixtures are prepared by weighing into a 3-inch test-tube the required amount of Se, heating till the Se is thoroughly fused, allowing to cool, adding the S and heating over a low flame just sufficiently hot to allow thorough mixing with a glass rod. As the material cools it may be gathered on the rod, removed, and cut into small fragments, which may be kept permanently in the stoppered tube. A gram or two is sufficient for examining a hundred preparations.

For use with the microscope a small piece of the mixture and a little of the mineral powder are heated on a glass slip under a cover-glass over a small flame till the mixture is fluid. The powder and liquid are then mixed and pressed into a thin film. The film is then heated during 15 to 30 seconds till bubbles begin to appear, again pressed thin and cooled. If care is taken no appreciable amount of sulphur will be vaporized from the film.

In the preparation of the mixtures, artificially crystallized sulphur should be used. Flowers of sulphur is satisfactory if it contains no mechanical impurities. The powdered or fused selenium furnished for this investigation by three dealers has been found to be sufficiently (better than 99.7 per cent) pure. It was tested by determining the refractive index of the glass made from the samples, and of that made from different fractions of the distilled selenium, and from precipitated selenium. The extreme values obtained in lithium light were 2.712 and 2.718. Mechanical impurities were sought for under the microscope in thin films of the glass. They were removed from one sample by distillation in a bent test-tube. In case it is not convenient to determine the refractive index of the selenium directly, its purity may be tested under the microscope. A mixture of 73 per cent Se, 27 per cent S, has the refractive index of pure sphalerite for light of wave-length $635\mu\mu$. This is the equivalent wave-length of light transmitted by a thin film of this mixture. The test is made then by embedding the powder of colorless or amber-colored sphalerite* in the mixture and determining the relative refractive indices through a screen of the same mixture. If the slide has a temperature of 30° – 35° C, or if it is studied through a screen of 85 per cent Se, the sphalerite should have the higher refractive index.

The refractive index of a mixture, correct to ± 0.01 , may be found on the goniometer by cautiously melting the mixture in the angle between two narrow strips of glass joined firmly at

* One per cent Cd or $\frac{1}{4}$ per cent Fe raises the refractive index about .001. The presence of 1 per cent or more of Fe produces a deeper color. The presence of disturbing amounts of Cd is very rare and can be known by analysis.

the ends by melting. The glass strips should be about 4 or 5^{mm} wide, 2^{cm} long, and 1^{mm} thick, and should include an angle of 35° to 45°. Microscope object glass cut crosswise is suitable provided its sides are sufficiently nearly plane and parallel, in which case the reflections of a wire or cord 3^{mm} in diameter in front of a window at a distance of 10 feet are not distorted nor entirely separated when the reflections are seen parallel to the direction the glass is to be cut.

If the refractive index of the mixture in the prism is to equal that of the film in which the mineral is embedded, it is essential that the mixture be heated to 250° or more before it is put into the prism. This is especially true of a mixture that has been standing some time and is partly crystallized.

The refractive indices in Table I and on the chart were found in this manner. The probable error does not exceed $\pm .005$ except in the case of wave-lengths less than 625 $\mu\mu$ in mixtures containing more than 80 per cent Se, where absorption is very strong. Likewise, the probable error in the dispersion of a given mixture does not exceed $\pm .002$.

The mixtures containing less than 15 per cent Se crystallize so readily that they are not well adapted to accurate work. Certain liquids, having refractive indices from 1.80 to 2.10, which fill the gap between the sulphur-selenium mixtures and liquids already well-known will be considered in a subsequent paper.

Geophysical Laboratory and Geological Survey,
Washington, D. C., April 18, 1912.

ART. V.—*On the Asymmetry in the Distribution of Secondary Cathode Rays produced by X-rays; and its Dependence on the Penetrating Power of the Exciting Rays; by C. D. COOKSEY.*

It has been shown by Bragg and Madsen* that the amount of secondary β -radiation excited in various solids by γ -rays is not symmetrically distributed about a plane perpendicular to the direction of propagation of the γ -rays, but that the β -radiation which comes from the side from which the γ -rays emerge is greater than that coming from the side on which the γ -rays are incident. The same effect is observed, though to a less degree, in the case of secondary X-rays,† and the secondary cathode rays produced by X-rays,‡ and those produced by ultra-violet light.§ This lack of symmetry is less for soft γ -rays than for hard and still less for X-rays, which are usually considered as very soft γ -rays. The order of magnitude of the ratio of emergence to incidence radiation ranges all the way from 20:1 down to unity, depending on the nature of the radiations used and the substance in which the secondary rays are excited.

Since I first showed that this effect was true for the cathode rays produced by X-rays, I have been experimenting with a view to find how the ratio of emergence to incidence radiation depends on the hardness of the exciting rays. But with these rays the effect is so small at best, that the variations which might be produced by the widest possible variation in hardness of the primary are not likely to be much greater than the experimental errors always inherent in X-ray measurements. Some results which I at first obtained|| seemed to indicate that there was a slight increase in the ratio with an increase of hardness of the primary. But owing to the heterogeneity of the rays from an ordinary tube, and the difficulty, at that time, of sorting out and using rays of a single penetrating power, these results were not very convincing.

Since these results were obtained, however, the work of Prof. Barkla and others on "Fluorescent" X-radiations, a summary of which is to be found in the Phil. Mag. for Sept., 1911, page 396, has afforded a convenient means of obtaining homogeneous beams of X-rays of known penetrating powers over a wide range. It was by this means that the experiments described in the present paper were performed.

* Trans. Roy. Soc. South Australia, vol. xxxii, May, 1908.

† Bragg and Classon, loc. cit., Oct., 1908.

‡ Cooksey, Nature, vol. lxxvii, p. 509, 1908.

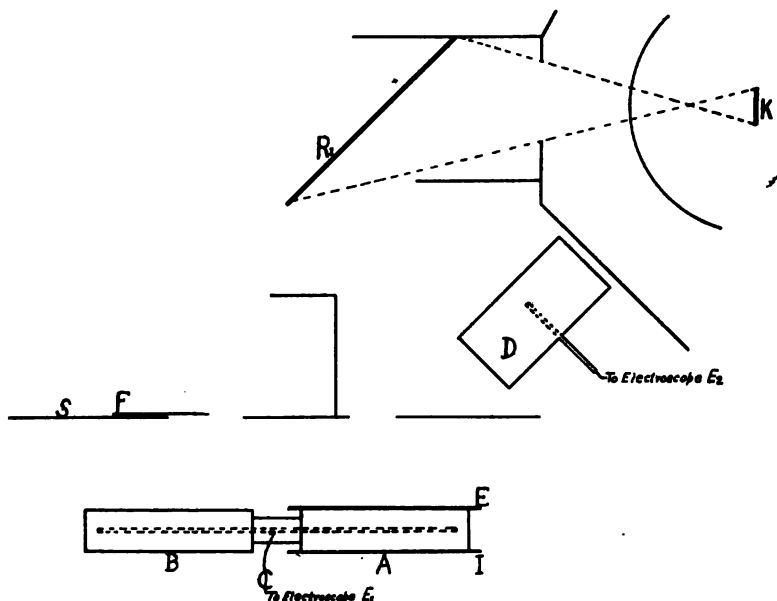
§ Stuhlmann, Phil. Mag., vol. xxii, p. 854, 1911.

|| Nature, vol. lxxxii, p. 128, 1909.

Apparatus and Method.

The apparatus used is shown in the accompanying diagram and was a modified form of the apparatus used in previous experiments.*

The X-ray tube was completely enclosed in a thick lead box, and the rays, proceeding from the anti-cathode, K, passed through a window in the box and fell on the radiator, R₁,



which consisted of a metal known to give off fluorescent X-rays. The fluorescent rays from R₁ passed through windows in a lead screen, S, into the ionization chambers, A and B, which were maintained at potentials of +240 and -240 volts respectively. A wire, C, passing into A and B through insulating plugs was connected to the gold leaf of a sensitive electroscope, E₁, of the type described by R. T. Beatty.† The two quadrants of this electroscope were connected to A and B respectively, and the wire, C, was normally connected to earth. A third ionization chamber, D, received some of the rays from R₁ and was always connected to earth. A wire running from the inside of D and insulated from it connected with the gold leaf of a second electroscope, E₂, of

* This Journal, vol. xxiv, p. 285, 1907.

† Phil. Mag., vol. xiv, p. 604, 1907.

the ordinary type. This wire and gold leaf could be charged to any convenient potential; and the rate of fall of the gold leaf when the rays were turned on, served as a measure of the intensity of the rays from R_1 . Each electroscope was fitted with a microscope and scale for observing the motion of the gold leaf. A lead screen, F , could be slid across the window in front of B by means of a screw, giving a very fine adjustment of the amount of the radiation entering this chamber.

The chambers, A and B , consisted of brass cylinders about 10 cm^{a} in diameter and 2.2 cm^{a} long, covered with lead on the outside. The ends of B were covered with aluminium foil. The end of the wire, C , which entered A , terminated in a wire ring of a diameter slightly less than the inside diameter of A , and lying in a plane perpendicular to the axis of A . The opening in the screen, S , opposite A was so adjusted that no part of the beam from R_1 could fall on the ring or on the walls of A .

Brass plate holders, E and I , covered the ends of A . These plate holders were made exactly alike to be interchangeable. Each one consisted of two square brass plates, held together with screws, and having a circular hole bored through their center of about the same diameter as the inside of A . These plate holders could be slid on and off the ends of A in somewhat the same manner as a camera plate holder, and stops were so placed that they would always come to the same position, with the center of the hole on the axis of A .

In order to produce the emergence cathode rays, it was necessary to pass the rays from R_1 through a plate of some metal in which cathode rays are produced in sufficient numbers to be easily measured. As these metals are relatively opaque to X-rays it was necessary to use very thin sheets. Gold and silver were fixed upon for this purpose. The gold leaf was $0.8 \times 10^{-6}\text{ cm}^{\text{a}}$ thick and the silver leaf $1.8 \times 10^{-6}\text{ cm}^{\text{a}}$. Circular disks of aluminium about $0.012\text{ cm}^{\text{a}}$ thick were made with a diameter slightly larger than the holes in the plate holders, and on one side of each was laid a thin foil of one of the above metals, stuck on with a thin coat of vaseline. When thicker sheets of metal were wanted more foils could be added by first holding the disks, already covered with one foil, in the vapor of heated vaseline, and then laying them on the foil to be added. One of these disks covered with one of the metals, say gold, was then screwed between the two parts of each plate holder and the holders placed over the ends of A with the aluminium sides facing in.

When the tube was turned on, and the wire, C , insulated from the earth, there would be a motion of the gold leaf in the electroscope, E_1 , toward one or other of the quadrants, depend-

ing upon whether the ionization in A or B was more intense. By a suitable adjustment of the screen, F, the ionization in the two chambers could be made equal, when there would be no motion of the gold leaf. After this adjustment was made the tube was stopped, and the front holder, E, reversed so that the gold side faced into A. The leaf in the electroscope, E₁, was then charged to a potential of about 200 volts, and the tube again excited. When the leaf reached a certain division on the scale the wire, C, was again insulated, and after the leaf in E₁ had passed over a convenient number of scale divisions the tube was stopped. The position of the leaf in E₁ was then observed, and C connected to earth through a potentiometer, and a sufficient potential applied to keep the leaf at its observed position. Calling this potential a , we can take it as a measure of the excess of ionization in A over that in B. If e denotes the ionization produced by the emergence secondary rays from the gold, and e' by the emergence secondary rays from aluminium, we shall have

$$e - e' = ka$$

where k is a constant.

After this measurement was made the holder, E, was turned back with the aluminium face in, and the other holder, I, reversed so that the gold faced in. The tube was again excited, and the potential, b , acquired by the leaf in E, while the leaf in E₁ passed over the same interval as before, was measured. Denoting the ionization produced by the incidence secondary rays from the gold by i , and that by the incidence secondary rays from the aluminium by i' , we can write as before

$$i - i' = kb$$

Letting $e'/e = m$, and $i'/i = n$ we shall have

$$e/i = a/b (1 - n)/(1 - m)$$

where e/i is the ratio of the emergence secondary radiations produced in the gold by a certain beam of X-rays from R, to the incidence secondary radiations produced by the same beam after traversing the ionization chamber. In the light of the results obtained in a previous paper,* and owing to the fact that the ionization chambers used in the present work were only two-fifths as long as those used before, we may assume that the secondary X-rays from the metal produced a negligible amount of ionization in the chamber compared to that produced by the cathode rays from the metal.

No data are readily obtainable in regard to m , but it is known that the amount of cathode rays given out by aluminium

* This Journal, xxiv, p. 285, 1907.

is very small compared with the amount given out by metals of high atomic weight, such as gold and silver. Unless the ratio of emergence to incidence radiation is far different in aluminium from what it is in gold and silver, which is unlikely, the difference between m and n will be a quantity which we may neglect, and we may write for a sufficient approximation

$$e/i = a/b$$

The determination of e/i , as above described, was always repeated with the two plate holders reversed with respect to the ends of A, which should give the same result if both plates were the same. The values obtained, however, in the two cases differed very widely; much more than could be accounted for by the experimental errors. The only explanation seemed to be that, owing to dirt on the surface or variations in the thickness of the metal foils, one plate was more efficient in giving out cathode rays than the other. If this were the case both the incidence and emergence rays should be effected in the same ratio, and the geometric mean of the two determinations of e/i should give the same result. To test this, different pairs of plates were made and also more foils were added to the same plates, but no matter what the discordance was between the two values of e/i for a given pair of plates, the geometric mean of the value found when one plate was on the front of A and the other on the back, and the value when these positions were reversed, always gave the same result within the limits of error of the experiment.

This ratio, e/i , does not, however, give the true ratio of emergence to incidence effect for the same intensity of exciting rays owing to the fact that these were absorbed in the air of the ionization chamber and to some extent in the layer of the metal from which the cathode rays come. The ratio of the number of emergence cathode rays coming from a layer of the metal so thin that the exciting rays suffer no absorption in it to the number of incidence cathode rays coming from the same layer is the true value sought. Let this be designated by R . Let β be the coefficient of absorption of the cathode rays in the metal from which they come, λ_1 the coefficient of the exciting X-rays in the same metal, and λ_2 their coefficient in air. The number of emergence cathode rays produced in a layer of thickness dx at a depth x of the metal by X-rays of intensity I is equal to

$$KI dx$$

where K is some constant. If the intensity of the X-rays on entering the metal is I_0 , and the thickness of the plate z , the number of the emergence cathode rays which get out of this layer into the ionization chamber is equal to

$$KI_0 \epsilon^{-\lambda_1 x} \epsilon^{-\beta(t-x)} dx$$

and the total number getting out of the whole plate is

$$\begin{aligned} e &= KI_0 \epsilon^{-\beta t} \int_0^t \epsilon^{(\beta-\lambda_1)x} dx \\ &= \frac{KI_0 \epsilon^{-\beta t}}{\beta-\lambda_1} \left[\epsilon^{(\beta-\lambda_1)t} - 1 \right]. \end{aligned}$$

The X-rays after being absorbed in the plate on the front of A are absorbed by the air in A and by the plate on the back of A. Therefore the intensity of these rays after reaching a depth x of the second plate will be

$$I_0 \epsilon^{-\lambda_1 t} \epsilon^{-\lambda_2 t'} \epsilon^{-\lambda_1 x}$$

where t' is the length of the ionization chamber. Therefore the number of incidence cathode rays getting into the ionization chamber from the second plate of thickness t will be equal to

$$i = \frac{KI_0 \epsilon^{-(\lambda_1 t + \lambda_2 t')}}{R(\beta + \lambda_1)} \left[1 - \epsilon^{-(\beta + \lambda_1)t} \right]$$

The ratio of the number of emergence cathode rays entering A to the number of incidence cathode rays is therefore

$$e/i = R \frac{\beta + \lambda_1}{\beta - \lambda_1} \epsilon^{2\lambda_1 t + \lambda_2 t'} \left[\frac{\epsilon^{(\beta - \lambda_1)t} - 1}{\epsilon^{(\beta + \lambda_1)t} - 1} \right]$$

Since λ_1 is small compared to β , the most important part of this equation is $R \epsilon^{\lambda_2 t'}$. Designating the other factors by S we may write

$$R = \frac{e/i}{S \epsilon^{\lambda_2 t'}}$$

If we assume that the absorption coefficient of the cathode rays is proportional to the density of the absorbing material we can calculate the values of β from the values given by Sadler* for their coefficient in air.

Sadler† has measured the coefficients of absorption in air of the fluorescent radiations characteristic of copper and arsenic,

* Phil. Mag., vol. xxii, p. 447 1911.

† Loc. cit.

and he and Barkla* have shown that the ratio of the coefficients of any two fluorescent beams is constant for all absorbing substances in which these beams do not excite a fluorescent radiation. We can, therefore, calculate the values of λ_1 in air from those in aluminium and in air given by Barkla and Sadler.

The fluorescent rays used were those from chromium, iron, zinc, and tin, and with the exception of tin Barkla and Sadler† have measured their absorption coefficients in gold and silver. Their value for the coefficient of the rays from chromium in gold is unreliable according to their statement, but it will be seen that λ_1 is always so small with respect to β that an exact knowledge of this quantity is not important.

The absorption coefficients of the rays from tin in gold and silver are not given by the above writers, but may be obtained approximately from the constant ratio between absorption coefficients cited above. Tin rays, being more penetrating than those characteristic of silver and gold, will excite their fluorescent radiations and, therefore, will probably be less penetrating to these metals than the above calculation would indicate, but an inspection of the curves given by Barkla will show that the increase of absorption is not very great in this part of the spectrum, and it will be seen that the effect of λ_1 is negligible in the case of the rays from tin.

The accompanying tables give the value of the quantities occurring in the formula as calculated from the data given by Barkla and Sadler and the observed values of e/i in gold and silver. The last column gives the values of R as calculated from these results. Most of the values of e/i were obtained using only one sheet of metal foil, but in some cases more than one sheet was used. As the terms in the formula containing t drop out when t is equal to or greater than two sheets of the metal, and as no consistent variation with the thickness of the sheets was observed, the mean of *all* the values of e/i using more than one sheet and the resulting values of R are given separately in the tables following the greater value of t .

It is at once apparent from the tables that the ratio of emergence to incidence cathode rays does not vary with the penetrating power of the exciting X-rays in the range of penetrating powers used; that is, for an increase of absorptibility as measured in aluminium of about 8000 per cent there is no measurable variation in the ratio.

It is interesting to note in this connection the values of the ratio compared to those found by Stuhlmann for the cathode rays produced by ultra-violet light. The value he gives for

* Phil. Mag., vol. xvii, p. 739, 1909.

† Loc. cit.

GOLD.

Radiator λ_i in Al	λ_i	λ_s	$\beta \times 10^{-4}$	$t \times 10^3$ cms.	S	$e^{\lambda_i t'}$	$Se^{\lambda_s t'}$	e/i Obs.	R
Chromium 367	9780·	0·0321	70·0	$> 0·8$	1·03	1·07	1·10	1·30	1·18
				$= 1·6$	1·03		1·10	1·34	1·22
Iron 239	7070·	0·0209	66·0	$> 0·8$	1·01	1·05	1·06	1·31	1·24
				$= 1·6$	1·02		1·07		
Zinc 106·3	3438·	0·0093	57·5	$> 0·8$	1·01	1·01	1·02	1·21	1·19
				$= 1·6$	1·01		1·02	1·25	1·23
Tin 4·33	106·4	0·0004	10·7	$> 0·8$	1·00	1·00	1·00	1·15	1·15
				$= 1·6$	1·00		1·00	1·16	1·16

SILVER.

Chromium 367	6095·	0·0321	38·0	$> 1·8$	1·02	1·07	1·09	1·33	1·22
				$= 3·6$	1·03		1·10	1·40	1·27
Iron 239	4000·	0·0209	35·8	$> 1·8$	1·03	1·05	1·08	1·31	1·21
				$= 3·6$	1·02		1·07		
Zinc 106·3	1830·	0·0093	31·4	$> 1·8$	1·02	1·01	1·03	1·24	1·20
				$= 3·6$	1·01		1·02		
Tin 4·33	23·02	0·0004	5·75	$> 1·8$	1·00	1·00	1·00	1·23	1·23
				$= 3·6$	1·00		1·00	1·23	1·23

silver is 1·07, and for platinum, which seems to behave, for X-rays at least, about the same as gold, 1·17. This is about the same as the mean of all the values which I have obtained for gold. His value for silver is somewhat less than the mean of my determinations. If the mechanism of production of cathode rays is the same with ultra-violet light as it is with X-rays, the ratio of emergence to incidence effect does not seem to vary much over a range of absorbability corresponding to the X-rays from tin up to that corresponding to ultra-violet light.

Summary.

The ratio of emergence to incidence cathode rays produced in gold and silver by beams of fluorescent secondary X-rays has

been measured with the object of finding the dependence of the ratio on the penetrating power of the exciting rays.

The fluorescent secondary X-rays from tin, zinc, iron, and chromium were used as exciting rays, representing an increase in absorbability as measured in aluminium of about 8000 per cent between tin and chromium.

After allowing for the absorption of the exciting rays in the layer of the metal from which the cathode rays come and in the air of the ionization chamber, it was found that there was no definite variation in the ratio of emergence to incidence effect.

In closing I wish to express my thanks to Professor H. A. Bumstead for the interest he has taken in the work.

Sheffield Scientific School, Yale University,
New Haven, Conn., March, 1912.

ART. VI.—*A Derivation of the Fundamental Relations of Electrodynamics from those of Electrostatics ;* by LEIGH PAGE.

MAXWELL's electrodynamic equations are based upon three experimental laws : (1) the inverse square law for the electric force between two point charges relatively at rest ; (2) Ampere's law for the force between current elements, or its equivalent ; (3) Faraday's law of current induction. Helmholtz gave a derivation of Faraday's law from Ampere's law by means of the principle of conservation of energy, which, however, has been shown to be erroneous.* Indeed, it has been impossible by any of the methods heretofore used to derive the electrodynamic equations without making use of all three of these experimental laws.

The object of this paper is to show, that if the principle of relativity had been enunciated before the date of Oersted's discovery, the fundamental relations of electrodynamics could have been predicted on theoretical grounds as a direct consequence of the fundamental laws of electrostatics, extended so as to apply to charges relatively in motion as well as to charges relatively at rest. Of course, only that part of the theory derived from the principle of relativity that is independent of any *a priori* knowledge of the electrodynamic equations, will be made use of. That is to say, we will use only the kinematics of relativity :—to use the dynamics of relativity, which is derived from the electrodynamic equations, would be to reason in a circle.

A material system is defined as an aggregate of material bodies having no relative motion, and showing no linear acceleration or angular velocity as a whole. Suppose now that we have any number of these systems moving in various directions and with various velocities relative to one another. The principle of relativity states that there are no experimental methods, practical or ideal, of distinguishing one such system as being marked out as different from all the others. In other words, if there is an ether, there exist no experimental methods by which we can find out which of these various systems is at rest relative to the ether.

One of the most obvious consequences of this principle is that the velocity of light, as measured in any one system, must be the same as measured in any other system. Otherwise there would be accessible to us an experimental method of locating the luminiferous ether, which is in contradiction to

* Maxwell's "Electricity and Magnetism," 8d edition, vol. ii, p. 192.

the principle of relativity. As a mathematical consequence of the fact that the velocity of light must be the same as observed from different systems, Einstein, in his celebrated paper* in the *Annalen der Physik*, has derived a set of space time transformations, which, because they were first deduced by Lorentz from entirely different considerations, usually go by his name.

Einstein starts off by a consideration of the meaning that can be attached to time simultaneity at two different points in any one system. Suppose A and B to be two widely separated places in the same system. An observer at A is watching certain phenomena in his immediate neighborhood, while an observer at B is watching certain other phenomena in his (B's) immediate neighborhood. They wish to compare the times of their observations. Obviously they must be provided with synchronous clocks. How are these clocks to be set synchronously? Let A send a light wave toward B when A's clock indicates the time t_A . This light wave reaches B at a time t_B on B's clock, and is returned to A by instantaneous reflection, reaching A at the time t'_A as indicated on A's clock. Since the measured value of the velocity of light is the same in all systems, and the same in all directions in any one system, the clocks at A and B will be synchronous when, and only when, $t_B = \frac{1}{2}(t_A + t'_A)$. Applying this definition of synchronism to two systems in motion relative to one another, Einstein is led to a set of transformations which show that the time at a point P in one system is a function not only of the time at a point Q in the other system, but also of the relative positions of the points P and Q.

When applied to the measurement of distances, these transformations show that a bar which is fixed in the first system with its axis parallel to the direction of relative motion of the two systems, and which has a length l as measured by an observer in the first system, will appear to have a shorter length when measured by an observer in the second system. This apparent shortening is not surprising when we consider the method used in measuring a body which is in motion relative to the observer. Let AB be a bar which has a velocity relative to the observer in the direction AB. In order to measure the length of the bar, the observer must mark the positions of the two ends of the bar at the *same instant*, and then measure the distance between these two marks. If he marks the position of the end B a little earlier than he marks the position of the end A, his measurement will be too short. Hence we see that space measurements as well as time measurements on moving systems, depend on the definition of simultaneity at different points of the same system.

* *Annalen der Physik*, xvii, 891, 1905.

Let $K(o)$ denote the earth's system at any instant. Then $K(v)$ denotes a system with velocity v relative to the earth.

Let XYZ be a set of orthogonal right-handed axes fixed in the earth's system, and so oriented that $K(v)$ has a velocity v in the positive z direction.

Let $X'Y'Z'$ be a set of orthogonal right-handed axes fixed in system $K(v)$ and mutually parallel to XYZ .

Unprimed letters denote quantities as measured in the earth's system, and primed letters denote the same quantities as measured in the system $K(v)$.

Then the space time transformations between $K(o)$ and $K(v)$ take the form :

$$\begin{aligned} t' &= \frac{t - \frac{v}{c^2} z}{\sqrt{1 - \frac{v^2}{c^2}}} & t &= \frac{t' + \frac{v}{c^2} z'}{\sqrt{1 - \frac{v^2}{c^2}}} \\ x' &= x & x &= x' \\ y' &= y & y &= y' \\ z' &= \frac{z - vt}{\sqrt{1 - \frac{v^2}{c^2}}} & z &= \frac{z' + vt'}{\sqrt{1 - \frac{v^2}{c^2}}} \end{aligned}$$

where c denotes the velocity of light, and where the time epochs are so chosen that the times at the respective origins of the two systems are zero when these origins coincide.

Let a particle have the velocity V relative to $K(o)$, and V' relative to $K(v)$. Let V_x, V_y, V_z be the components of V , and V'_x, V'_y, V'_z the components of V' . Then the following kinematical transformations follow at once by taking the time derivatives of the space time transformations, with consideration of the relation

$$\begin{aligned} dt \sqrt{1 - \frac{V^2}{c^2}} &= dt' \sqrt{1 - \frac{V'^2}{c^2}} \\ \frac{V'_x}{V_x} &= \frac{V'_y}{V_y} = \frac{\sqrt{1 - \frac{V'^2}{c^2}}}{\sqrt{1 - \frac{V^2}{c^2}}} = \frac{1 + \frac{vV'_z}{c^2}}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{\sqrt{1 - \frac{v^2}{c^2}}}{1 - \frac{vV_z}{c^2}} \\ V'_x &= \frac{V_x - v}{1 - \frac{vV_x}{c^2}} & V_x &= \frac{V'_x + v}{1 + \frac{vV'_x}{c^2}} \end{aligned}$$

$$\frac{\dot{V}_x'}{\left(1 - \frac{V'^2}{c^2}\right)^{1/2}} = \frac{\dot{V}_x - \frac{v}{c^2} [\mathbf{V} \cdot \dot{\mathbf{V}}_x - \mathbf{V}_x \cdot \dot{\mathbf{V}}]}{\left(1 - \frac{V^2}{c^2}\right)^{1/2} \sqrt{1 - \frac{v^2}{c^2}}}$$

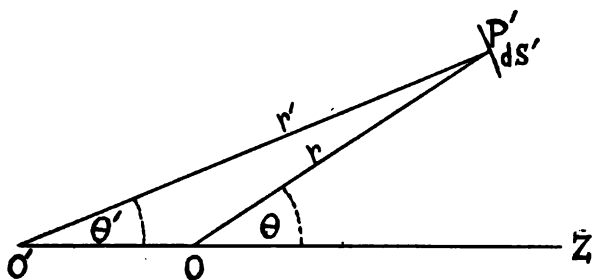
and similarly for \dot{V}_y

$$\left(\frac{\dot{V}_x'}{\left(1 - \frac{V'^2}{c^2}\right)^{1/2}}\right)^2 = \left(\frac{\dot{V}_x}{\left(1 - \frac{V^2}{c^2}\right)^{1/2}}\right)^2$$

Moving Charges.

We can represent the field due to a charged particle which is at rest relative to the observer by radial lines of force so drawn that equal solid angles contain the same number of lines of force. Then we can define the intensity at any point as having the direction of the line of force at that point and as

FIG. 1.



being proportional, in magnitude, to the density of the lines of force at that point. Now let us extend this definition of intensity to charges which are moving relative to the observer. Consider a charge e at the point O' (fig. 1) in $K(v)$. Let dS' be an elementary surface fixed in $K(v)$ at P' , and perpendicular to $O'P'$. Let $O'P' = r'$, and the angle between $O'P'$ and the Z' axis be θ' . Then E' , the force at P' as measured in $K(v)$, will be $\frac{e}{r'^2}$. We wish to find the force E due to e ,

at a point P in $K(o)$, when P coincides with P' . On account of the different definitions of simultaneity in the two systems $K(v)$ and $K(o)$, when P' and P coincide the charge e as viewed from $K(o)$ will be at some point O not coincident with O' . Let $OP = r$, and let the angle between OP and the Z axis be θ . The space time transformations give the relations

$$r' = \frac{\sqrt{1 - \frac{v^2}{c^2} \sin^2 \theta}}{\sqrt{1 - \frac{v^2}{c^2}}} r$$

$$\sin \theta' = \frac{\sqrt{1 - \frac{v^2}{c^2}}}{\sqrt{1 - \frac{v^2}{c^2} \sin^2 \theta}} \sin \theta$$

$$\cos \theta' = \frac{1}{\sqrt{1 - \frac{v^2}{c^2} \sin^2 \theta}} \cos \theta$$

The direction of the lines of force, as viewed from $K(o)$, and hence the direction of the intensity, will be OP , and *not* $O'P'$. Now dS' as viewed from $K(o)$ will not be perpendicular to OP . Let dS be the component of dS' , as viewed from $K(o)$, which is perpendicular to OP . Then a short calculation gives

$$dS' = \frac{1}{\sqrt{1 - \frac{v^2}{c^2} \sin^2 \theta}} dS$$

Now the density of the lines of force at P in $K(o)$ is to the density of the lines of force at P' in $K(v)$, at the instant when P and P' coincide, as dS' is to dS ; that is to say in the ratio $1 : \sqrt{1 - \frac{v^2}{c^2} \sin^2 \theta}$. Hence we have

$$\frac{E}{E'} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2} \sin^2 \theta}}$$

$$\text{But } E' = \frac{e}{r'^2} = \frac{e}{r^2} \left(1 - \frac{v^2}{c^2}\right) \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)$$

$$\text{Therefore } E = \frac{e}{r^2} \left(1 - \frac{v^2}{c^2}\right) \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}$$

I

The force E , as already noted, has the direction of the line of force through P , as observed in $K(o)$; that is, the direction OP , where O is the apparent position of the charge to an observer in $K(o)$ at the instant considered.

Thus, by means of the principle of relativity we have been able to derive from the laws of electrostatics, with considerable ease, an expression which Heaviside has derived from the electromagnetic equations only by the use of somewhat complicated mathematical processes.

The relations between the components of E at P and E' at P' follow at once from the expressions we have already derived.

$$E_x = \frac{E'_x}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$$E_y = \frac{E'_y}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$$E_z = E'_z$$

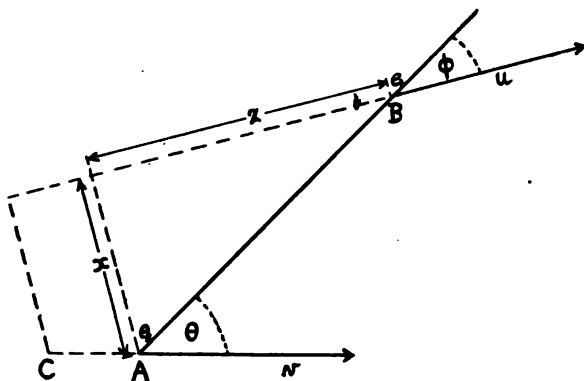
Force between Current Elements.

We can consider a current as made up of a given quantity of positive electricity moving with a given drift velocity along the wire in the direction of the current, and some other given quantity of negative electricity moving with some other given drift velocity in the direction opposite to that of the current. Let u_1 be the velocity of the positive electricity, and u_2 that of the negative electricity. Let λ_1 be the linear density, or the quantity of moving positive electricity per unit length of wire, and λ_2 the quantity of moving negative electricity per unit length of wire. Consider an element of the wire of length ds . Then we can define a current element as $(\lambda_1 u_1 + \lambda_2 u_2) ds$. Now this element of wire is as a whole uncharged. So there must be a quantity of positive electricity $(k - \lambda_1) ds$, and a quantity of negative electricity $(k - \lambda_2) ds$ at rest in the element, k being some constant. As the current is due to that part of the charge in the wire which is in motion, our problem reduces to a consideration of the forces between two charges both of which are moving relative to the observer.

In order to make our reasoning as simple as possible, we shall confine ourselves to currents lying in the same plane. There is no difficulty in extending the reasoning to currents which do not lie in the same plane, but in that case the demonstration becomes a little more complicated.

At a given instant in $K(o)$, two charged bodies (fig. 2), one at A and the other at B, have velocities relative to $K(o)$ of v and u cm./sec. respectively. $AB = r$. Choose axes XZ so that z is parallel to u . Let the origin be at B. We wish to find the force on the charged body at B, due to the other charged body. To find this force we must observe from the

FIG. 2.



system $K(u)$. But according to the time synchronism of $K(u)$, when the one charged body is at B, the other will not be at A. It will be at C, a point whose coordinates are found to be

$$z = -\frac{r \cos \phi}{1 - \frac{uv \cos (\theta - \phi)}{c^2}} \quad x = -\frac{r \sin \phi - r \frac{uv}{c^2} \sin \theta}{1 - \frac{uv \cos (\theta - \phi)}{c^2}}$$

These distances, as measured in $K(u)$, are (the primes refer to $K(u)$),

$$z' = -\frac{r \cos \phi \sqrt{1 - \frac{u^2}{c^2}}}{1 - \frac{uv \cos (\theta - \phi)}{c^2}} \quad x' = -\frac{r \sin \phi - r \frac{uv}{c^2} \sin \theta}{1 - \frac{uv \cos (\theta - \phi)}{c^2}}$$

and the distance between the charges is

$$r' = \frac{r}{1 - \frac{uv \cos (\theta - \phi)}{c^2}} \left\{ 1 - 2 \frac{uv}{c^2} \sin \phi \sin \theta + \frac{u^2 v^2}{c^4} \sin^2 \theta - \frac{u^2}{c^2} \cos^2 \phi \right\}^{\frac{1}{2}}$$

Applying I and reducing, we get

$$F_x' = \frac{e_1 e_2 \left(1 - \frac{v^2}{c^2}\right) \left(\sin \phi - \frac{uv}{c^2} \sin \theta\right)}{r^2 \left(1 - \frac{u^2}{c^2}\right)^{\frac{1}{2}} \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

$$F_z' = \frac{e_1 e_2 \left(1 - \frac{v^2}{c^2}\right) \cos \phi}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}.$$

Let F_x and F_z be the forces as measured in K (ϕ) that must be applied to the charge at B in order to produce the same effect as F_x' and F_z' . Then

$$F_x = \frac{e_1 e_2 \left(1 - \frac{v^2}{c^2}\right) \left(\sin \phi - \frac{uv}{c^2} \sin \theta\right)}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

$$F_z = \frac{e_1 e_2 \left(1 - \frac{v^2}{c^2}\right) \cos \phi}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

Now replace e_1 by a current element $(\lambda_1 u_1 + \lambda_2 u_2) ds$. In this current element there is at rest the positive electricity $(k - \lambda_1) ds$, and the negative electricity $(k - \lambda_2) ds$. Consider the positive electricity $\lambda_1 ds$ which is moving, and a portion $\lambda_2 ds$ of the negative electricity which is at rest. Then the components of the force due to e_2 on the negative electricity $\lambda_2 ds$ at rest will be

$$F_x = \frac{-\lambda_2 e_2 \left(1 - \frac{v^2}{c^2}\right) \sin \phi ds}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

$$F_z = \frac{-\lambda_2 e_2 \left(1 - \frac{v^2}{c^2}\right) \cos \phi ds}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

But the components of the force due to e_2 on the positive electricity $\lambda_1 ds$ in motion is, as we have just found,

$$F_x = \frac{\lambda_1 e_1 \left(1 - \frac{v^2}{c^2}\right) \left(\sin \phi - \frac{u_1 v}{c^2} \sin \theta\right) ds}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

$$F_z = \frac{\lambda_1 e_1 \left(1 - \frac{v^2}{c^2}\right) \cos \phi ds}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

Combining, we have left the force

$$-\frac{\lambda_1 e_1 u_1 v}{c^2} \left(1 - \frac{v^2}{c^2}\right) \sin \theta ds$$

$$r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}$$

in the X direction.

Proceeding in the same manner, we find the total force on the current element at B due to the moving charge at A is

$$F_x = \frac{-\frac{e_2 v i_1}{c} \sin \theta ds \left(1 - \frac{v^2}{c^2}\right)}{r^2 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

where i_1 is the current in electromagnetic units. As the drift velocity of the charges constituting a conduction current in a wire is certainly small compared with the velocity of light, we can place the factor

$$\frac{\left(1 - \frac{v^2}{c^2}\right)}{\left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}}$$

equal to unity.

If we replace e_1 by a current element, we will find for the total force exerted by the current element $i_1 ds_1$ at A on the current element $i_2 ds_2$ at B, as measured on the earth (system K (o)), the expression

$$F_x = - \frac{i_1 i_2 \sin \theta ds_1 ds_2}{r^2}$$

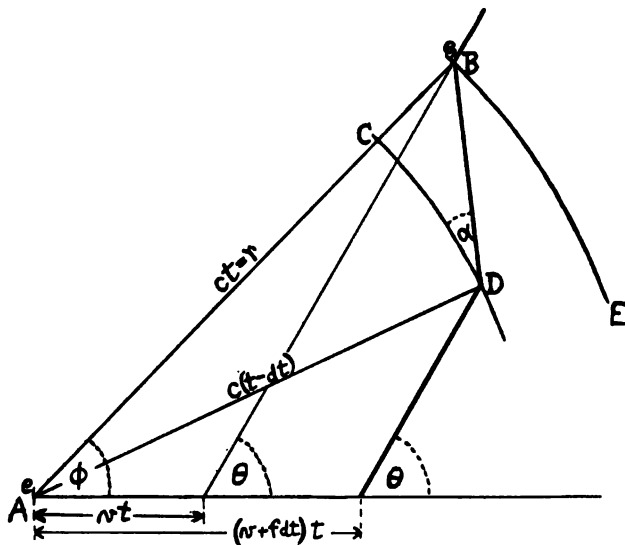
where i_1 and i_2 are measured in electromagnetic units.

This expression gives all the forces between currents, and also the induced current phenomena due to moving a closed circuit through a so-called magnetic field. The induced current effects produced in a secondary circuit by variation of the current in the primary are very simply treated as follows:

Faraday's Law.

Whenever a charged body is accelerated, it is obvious that the lines of force will be kinked. If the charged body is accelerated only for a very short time, these kinks will travel outwards in the form of a pulse. Now this pulse must have the same velocity relative to the system of the field inside the

FIG. 8.



pulse as it has relative to the system of the field outside the pulse. These two systems, however, may be chosen arbitrarily. Therefore the pulse must have the same velocity relative to all systems. The only velocity to satisfy this condition is the velocity of light. Hence the velocity of the pulse must be c .*

*This reasoning may be objected to on the ground that the pulse may expand as it moves outward: i. e., the outside of the pulse may have a greater velocity than the inside. But if this was true under certain conditions, it would be necessary to assume that the reverse was true under certain other conditions. So we would be forced to the most improbable conclusion that the inside of the pulse might outstrip and pass through the outside of the pulse.

Consider two charges e_1 and e_2 at A and B (fig. 3) respectively. Let the charge at B be at rest relative to the observer in $K(o)$, and the charge at A be moving to the right with the velocity v . While e_1 is at A the acceleration f is applied to it in the direction of its velocity v . Let $AB = r = ct$. BE is an arc with A as center and ct as radius, CD an arc with A as center and $c(t-dt)$ as radius. If, as before, we define the intensity as proportional to the density of the lines of force at the point considered, the force just to the left of B will be

$$F = \frac{e_1 e_2 \left(1 - \frac{v^2}{c^2}\right)}{r^3 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}} \cdot \frac{1}{\sin \alpha}$$

provided v is small compared to c . So the intensity at the same point due to e_1 will be

$$E = \frac{e_1 \left(1 - \frac{v^2}{c^2}\right)}{r^3 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}} \cdot \frac{1}{\sin \alpha}$$

If we denote by E_{\parallel} and E_{\perp} the components of E parallel to and perpendicular to the radius AB,

$$E_{\parallel} = \frac{e_1 \left(1 - \frac{v^2}{c^2}\right)}{r^3 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}} \quad E_{\perp} = \frac{e_1 \left(1 - \frac{v^2}{c^2}\right)}{r^3 \left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}} \cot \alpha$$

So we see that the component of the force parallel to the radius AB is continuous through the pulse.

Now $\cot \alpha = \frac{ft \sin \theta}{c}$ if $\frac{v}{c}$ is small.

$$\therefore E_{\parallel} = \frac{e_1 f}{rc^2} \frac{\left(1 - \frac{v^2}{c^2}\right)}{\left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}} \sin \theta$$

If we replace e_1 by a current element ids

$$E_{\parallel} = \frac{di}{dt} \frac{\sin \theta}{r} \frac{\left(1 - \frac{v^2}{c^2}\right)}{\left(1 - \frac{v^2}{c^2} \sin^2 \theta\right)^{\frac{3}{2}}} ds$$

in electromagnetic units.

If $\frac{v}{c}$ is small, this reduces to

$$E_i = \frac{di}{dt} \frac{\sin \theta}{r} ds$$

which is the expression for the induced electromotive force in one wire due to a variation of the current in another.

Conclusions.

Our object was to deduce the fundamental laws of electrodynamics,—the law for the force between currents, and the law governing current induction,—from those of electrostatics. We assumed that part of the theory derived from the principle of relativity which depends only upon the fact that the velocity of light must be the same as measured in different systems, and which depends in no way upon the electrodynamic equations. Then we extended the following conceptions of electrostatics to moving charges :

(1) To an observer at rest relative to a charge, the charge can be replaced by a field of lines of force radiating from the charge in such a way that equal solid angles contain equal numbers of lines of force.

(2) To an observer relative to whom the charge is in motion, as well as to an observer at rest relative to the charge, the electric intensity due to the charge is proportional to the instantaneous density of the lines of the force at the point considered.

By the means of these extensions of electrostatic conceptions to moving charges, we were able to deduce (a) the expression for the electric intensity due to a charge moving relative to the observer ; (b) Ampere's law, or its equivalent ; (c) Faraday's law, or its equivalent.

Viewed from another standpoint, the fact that we have been able, by means of the principle of relativity, to deduce the fundamental relations of electrodynamics from those of electrostatics, may be considered as some confirmation of the principle of relativity.

I want to express my thanks to Professor H. A. Bumstead for several valuable suggestions, and to Dr. H. M. Dadourian for his help and encouragement.

Sheffield Scientific School, March 7th, 1912.

ART. VII.—On the Hydrolysis of Esters of Substituted Aliphatic Acids; by W. A. DRUSHEL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxi.]

3. Ethyl α - and β -monochlorpropionates, ethyl α - and β -monobrompropionates and ethyl $\alpha\alpha$ -dibrompropionate.

It was shown by Walden* that the electrolytic dissociation of the brompropionic acids is very much influenced by the position of the halogen with respect to the carboxyl group. DeBarr,† in his investigation of the hydrolytic action of water upon halogen substituted fatty acids, found that the monohalogen substituted propionic acids are fairly stable in the presence of water at temperatures below 100° C., and that when decomposition takes place at a higher temperature (150° C.) the position of the halogen with respect to the carboxyl group has a marked effect upon the velocity of the reaction. The purpose of the present investigation was to study the influence of the position of the halogen on the velocity of the hydrolytic decomposition of the ethyl ester of chlor and brompropionic acids.

Preparation of Esters.—The ethyl α -chlorpropionate was obtained from Kahlbaum. The ethyl α -brompropionate was prepared by the method of Zelinsky.‡ The boiling points of the esters having indicated a fair degree of purity, they were analyzed for halogen. Small portions of the esters were weighed into flasks and decomposed with pure potassium hydroxide by warming on the steam bath for twenty-four hours. The solutions were then neutralized with nitric acid, diluted to definite volumes and the halogen estimated gravimetrically in aliquot portions. Chlorine found, I 26.28 per cent, II 25.91 per cent, mean 26.10 per cent; chlorine calculated for $\text{CH}_3\text{CHCl.COOCH}_2\text{H}_5$, 25.96 per cent. Bromine found, I 44.37 per cent, II 44.29 per cent, mean 44.33 per cent; bromine calculated for $\text{CH}_3\text{CHBr.COOCH}_2\text{H}_5$, 44.18 per cent.

The β -halogen substituted propionic esters were prepared by a modification of Richter's method§ for the preparation of β -halogen substituted propionic acids, which apparently had not heretofore been used for the preparation of the esters. The process for the preparation of the acids depends upon the direct replacement of iodine in β -iodopropionic acid in water solution by chlorine or bromine. In this process the iodine is said to separate out as free iodine. To prepare the correspond-

* Walden, *Zeitschr. f. phys. Chem.*, x, 650.† DeBarr, *Am. Chem. Jour.*, xxii, 333.‡ Zelinsky, *Ber.*, xx, 2026.§ Richter, *Zeitschr. f. Chem.*, 1868, 449–451.

ing ethyl esters, pure ethyl β -iodopropionate was dissolved in about five times its volume of chloroform and chlorine or bromine added in excess, keeping the temperature of the mixture below 50°C . by means of a water bath. Under these conditions the iodine is readily replaced by chlorine or bromine with the formation of considerable quantities of chloride or bromide of iodine and the liberation of much free iodine. The chloride or bromide of iodine was removed by shaking the chloroform solution of ester with water, and the free iodine was then removed by washing with dilute cold sodium carbonate solution and again with water. The chloroform solution of the new ester was dried over calcium chloride and the chloroform removed by warming on the steam bath. The esters so prepared were further purified by fractional distillation under diminished pressure. The β -chlorpropionic ester boiled at 162°C . at atmospheric pressure, and the β -brompropionic ester at 85°C . under a pressure of 25^{mm} . These esters on analysis by the previously described method gave the following results: Chlorine found, I 26.07 per cent, II 25.93 per cent, III 26.00 per cent, mean 26.00 per cent; calculated for $\text{CH}_3\text{Cl.CH}_2\text{COOC}_2\text{H}_5$, 25.96 per cent. Bromine found, I 44.10 per cent, II 44.20 per cent, III 44.10 per cent, mean 44.13 per cent; calculated for $\text{CH}_3\text{Br.CH}_2\text{COOC}_2\text{H}_5$, 44.18 per cent.

Ethyl $\alpha\alpha$ -dibrompropionate was prepared by a modification of the method of Philippi, Tollens.* In this method it is recommended that 9 parts of bromine be heated with 4 parts of propionic acid in a sealed tube at 190°C . to 220°C . for 24 hours, that the hydrobromic acid formed be removed, 9 more parts of bromine be added and the mixture heated for 48 hours at 190°C . to 220°C . A satisfactory yield of $\alpha\alpha$ -dibrompropionic acid was obtained by heating at 160°C . for two intervals of 6 hours each. Subsequently it was found that the first atom of hydrogen in propionic acid is completely replaced by bromine by heating at 160°C . for two hours. The purified dibrompropionic acid was esterified with absolute alcohol and dry hydrochloric acid in the usual manner. The ester obtained by this method boiled between 102°C . and 103°C . at 38^{mm} , and on analysis for bromine gave the following results: Bromine found, I 61.57 per cent, II 61.54 per cent; bromine calculated for $\text{CH}_3\text{CBr}_2\text{COOC}_2\text{H}_5$, 61.51 per cent.

Hydrolysis of Esters.—The ethyl esters of the monohalogen propionic acids were found to be soluble in water only to the extent of about 4^{cm^3} per liter, and the ethyl ester of $\alpha\alpha$ -dibrompropionic acid was found to be much less soluble, making it impossible to dissolve enough of this ester in decinormal acid to make satisfactory velocity measurements even at 60°C . In

* Philippi, Tollens, Ann. d. Chem. u. Pharm., clxxi, 315.

50 per cent acetone or alcohol the solubility of this ester is no greater than that of the monohalogen propionic acid esters in water. The presence of this amount of acetone or alcohol was found to retard the velocity of the hydrolysis so that no satisfactory results could be obtained. In the case of the monohalogen propionic esters 1^{cm} of each ester was dissolved in 250^{cm} of decinormal hydrochloric or hydrobromic acid previously warmed in the thermostat to the required temperature. As soon as the ester was completely dissolved 25^{cm} of the reaction mixture were titrated with decinormal barium hydroxide, using phenolphthalein as an indicator. Subsequent tritrations were made at the time intervals indicated in the tables, and the final titrations usually after the lapse of 12 to 14 days. In order to ascertain if any halogen was liberated in the form of free halogen acids from the esters or the halogen propionic acids resulting from the hydrolysis of the esters, titrations were made with decinormal silver nitrate at the time when the equilibrium was apparently reached. It was found that at 25° C. and 35° C. there was no apparent decomposition in this direction in the time required for all except the final titrations, and in these there was only a little decomposition observed at 35° C. and none at all at 25° C. The necessary correction was applied where there appeared an appreciable increase in the concentration of the halogen acid. At 50° C. the last titration, preceding the equilibrium titration, was made in each case within 10 hours of the beginning of the reaction. In the ethyl β -chloropropionate and the ethyl α - and β -bromopropionates as much as 2 per cent or 3 per cent of the halogen was set free as halogen acid, for which corrections were made accordingly. From these titrations the velocity constants recorded in Table I were calculated by using the well-known titration formula for monomolecular reactions: $K = \frac{2.3}{t} [\log (T_{\infty} - T_0) - \log (T_{\infty} - T_n)]$,

where T_0 is the initial titration, T_{∞} the final titration, and T_n the intermediate titrations, all expressed in cubic centimeters of decinormal barium hydroxide, and t is time in minutes between the titrations T_0 and T_n .

It was thought desirable also to make hydrolysis measurements in the absence of any added catalyzing acid. In this case the reactions proceed very slowly at first but with increasing velocity as the concentration of the acid liberated becomes greater. The velocity of the hydrolytic decomposition of the esters is accelerated by the halogen substituted propionic acids resulting from the hydrolysis of the esters and by the halogen acids subsequently set free by the hydrolysis of the halogen substituted propionic acids. This second accelerating effect becomes very prominent after the hydrolysis has proceeded for

some time, but when the hydrolysis is made in the presence of an initial decinormal concentration of halogen acid the accelerating effect of the halogen substituted propionic acid and of the subsequently liberated halogen acid is negligible in comparison to the accelerating effect of the added catalyzing halogen acid. By making occasional titrations with decinormal silver nitrate, the amount of halogen acid liberated in the secondary reaction was ascertained. The results obtained in the absence of any added catalyzing acid are recorded in Tables II and III.

TABLE I.

Ethyl esters of halogen substituted propionic acid in N/10 hydrochloric or hydrobromic acid.

Ethyl propionate		Ethyl α -chlor- propionate		Ethyl α -brom- propionate		Ethyl β -chlor- propionate		Ethyl β -brom- propionate	
Time in min.	10°K	Time in min.	10°K	10°K	10°K	Time in min.	10°K	10°K	10°K
A. At 25° C.									
60	70.3	420	28.8	21.3			9.6	(8.40) *	
360	71.8	1330	30.0	21.2			9.9	8.18	
600	70.2	1900	29.3	20.6			(10.6) *	8.12	
1380	70.5	2790	29.3	20.3			9.8	8.12	
2220	69.2	4215	28.1	21.6			9.8	8.16	
2800	70.7	4800	27.2	21.5			9.7	8.16	
		5700	27.0	20.9			9.7	8.17	
	70.45		28.5	21.06			9.76	8.15	
B. At 35° C.									
200	177.9	180	57.2	39.4			25.0	22.2	
260	177.4	360	56.5	38.3			23.3	21.4	
380	177.4	510	58.3	41.0			24.3	22.4	
500	177.2	1380	57.4	39.3			23.8	21.0	
705	177.1	1560	57.2	39.6			23.8	21.4	
1410	176.8	1800	55.8	38.3			24.4	21.3	
		1980	56.3	37.8			23.1	21.5	
	177.3		56.9	38.9			23.9	21.6	
C. At 50° C.									
20	534	20	186.1	92.5	110	86.5	52.3		
35	541	50	192.5	94.8	180	85.2	53.4		
50	529	110	181.2	96.0	300	89.0	56.3		
80	541	180	185.7	90.0	420	86.0	56.7		
110	537	300	195.8	90.3	580	83.8	53.8		
180	527	420	183.4	91.5					
300	528						86.1	54.5	
	533.8		187.4	92.5					

* Not included in the average.

TABLE II.

Esters in water alone.

Ethyl propionate		Ethyl α -chlor- propionate		Ethyl α -brom- propionate		Ethyl β -chlor- propionate		Ethyl β -brom- propionate	
Time in hr.	(α) % hydr.	Time in hr.	(α) % hydr.	(α) % hydr.	(α) % hydr.	Time in hr.	(α) % hydr.	(α) % hydr.	(α) % hydr.
A. At 35° C.									
163	0	49.5	3.0	2.6	51	9	2.8		
281	0.3	112.5	7.5	5.9	100	0.4	5.2		
385	0.7	163.5	10.9	10.9	166	1.1	9.7		
475	1.2	281	20.1	20.4	270	2.1	18.0		
573	1.8	385	28.8	31.7	360	2.7	26.3		
		475	36.2	45.5	458	3.4	36.2		
		573	44.8						
B. At 50° C.									
24	0.1	24	5.2	6.4	52	2.1	22		
50	0.4	50	11.1	16.3	96	4.1	49		
121	1.9	77	18.2	33.1	120	5.3	65		
175.5	4.2	120	32	67.6	150	7.7	85		
200.5	5.7	144	40.5	85.4	175	10.1	119		
241	8.0	175	50.1	107	216	13.2	141		
336	19.2	200	57	122	240	17.2	168		
		310	67.4*	151†	310	22.4‡	175§		

TABLE III.—Summary.

Hydrolysis in N/10 HCl or HBr.

	Ethyl propionate	Ethyl α -chlor- propionate	Ethyl α -brom- propionate	Ethyl β -chlor- propionate	Ethyl β -brom- propionate
	10°K	10°K	10°K	10°K	10°K
At 25°C.	70.4	28.5	21.06	9.75	8.15
" 35°C.	177.3	56.9	38.9	23.9	21.6
" 50°C.	533.8	187.4	92.5	86.1	54.5

Hydrolysis in water alone.

	Time in hr.	(b) % hydr.	Time in hr.	(b) % hydr.	(b) % hydr.	(b) % hydr.	(b) % hydr.
At 35°C.	458	1.1	458	28.3	45.5	3.4	36.2
" 50°C.	335	19.2	310	85	100	13	99

(a) % hydr. denotes total acidity referred to the initial concentration of ester.

(b) % hydr. denotes ester hydrolyzed, corrected for halogen acid set free.

* In 310 hours 6.3% of the total chlorine of the ester was set free as HCl.

† In 310 hours 66% of the total bromine of the ester was set free as HBr.

‡ In 310 hours 9.4% of the total chlorine of the ester was set free as HCl.

§ In 310 hours 75.6% of the total bromine of the ester was set free as HBr.

Summary.—In the presence of decinormal hydrochloric or hydrobromic acid at temperatures not exceeding 35°C ., the ethyl esters of the halogen substituted propionic acids decompose almost quantitatively according to the equation: $\text{C}_2\text{H}_5\text{X}.\text{COOC}_2\text{H}_5 + \text{HOH} \rightarrow \text{C}_2\text{H}_5\text{X}.\text{COOH} + \text{C}_2\text{H}_5\text{OH}$. Below 35°C . the halogen substituted propionic acids decompose very slowly according to the equation: $\text{C}_2\text{H}_5\text{X}.\text{COOH} + \text{HOH} \rightarrow \text{HX} + \text{C}_2\text{H}_5\text{OH}.\text{COOH}$. When decomposition takes place in this direction the β position of the halogen favors the reaction.

When hydrogen is replaced by halogen in the acid group of ethyl propionate the velocity of hydrolysis in the presence of an added catalyzing acid is much less than that of ethyl propionate, but in the absence of any added catalyzer it is much greater than that of ethyl propionate. The position of the halogen with respect to the carboxyl group has a marked effect on the velocity of hydrolysis. Esters with halogen in the α position hydrolyze more rapidly than esters with the halogen in the β position when the hydrolysis is made in the presence of an added catalyzing acid; the same is true when the hydrolysis is made in the absence of any added catalyzing acid if corrections are applied for the halogen acids set free by the hydrolysis of the halogen substituted propionic acids.

ART. VIII.—*Some Suggested New Physiographic Terms* ;*
by DELORME D. CAIRNES.

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Introductory.
Definition of Terms.
Classification of Physiographic Processes.
Equiplanation.
Deplanation.
Applanation.
Conclusion.

Introductory.

THE introduction of a new scientific term is only justified when there is good reason to believe that its use will promote the special branch of science to which the term has reference. There is a somewhat widespread tendency to-day to overburden our technical vocabularies with long words of uncouth sound which are difficult not only to remember but also to pronounce, and which apparently serve mainly to complicate rather than simplify the study of the subject into which they are admitted. Instead of rendering the study of any particular branch of science unduly difficult, our endeavor should be to promote simplicity and clearness both in thought and expression. It is desirable, however, that a sufficient number of technical terms should be employed to allow of the concise and accurate description of the various phenomena to be considered. Whenever a fundamental distinction is recognized between processes, forces, or agents, which may be very different in their nature, and still may or may not tend to produce results that are easily confused, it promotes clearness of conception to employ definite terms to indicate the nice distinctions that have been found to exist.

Physiography is one of the most rapidly growing of the more youthful branches of science, and has, so far, fortunately escaped any considerable overcrowding of its vocabulary. In fact the greater number, if not all of the terms that have been suggested within the past few years, have been greatly beneficial in that they have added to our knowledge of the subject, and have materially helped to clarify our ideas concerning the various phenomena with which they are concerned. Among the more important of the terms that have been recently introduced might be mentioned,—nivation,† topographic uncon-

* By permission of the Director of the Geological Survey branch of the Department of Mines of Canada.

† The term nivation was proposed by F. E. Matthes in 1899, and has since been described by Hobbs and others. See :—Matthes, F. E., "Glacial Sculpture in the Bighorn Mts., Wyo.," Twenty-first Ann. Rep. U. S. Geol. Survey, Pt. II, 1899, pp. 173-190. Hobbs, W. H., "Characteristics of existing glaciers," 1911, pp. 18-23.

formity,* topographic adjustment,* superimposed youth,* and solifluction.† All these have not only proved particularly convenient, but have given us more clear-cut conceptions and have also had a decided influence in promoting closer field observations.

The suggestion of the definite name peneplain by Prof. Davis in 1889 for a thing previously considered in a general way for a number of years, vastly promoted its consideration, and greatly stimulated physiographic research. Investigations, discussions, and writings followed rapidly after the christening of the peneplain idea.

At the annual meeting of the Geological Society of America in Washington, D. C., during December, 1911, the writer proposed the term equiplanation‡ to include certain physiographic processes. Since that time a considerable number of inquiries, concerning this subject, have been received. As a consequence of the nature of these inquiries it has seemed advisable to write this essay, which is intended to be somewhat in the nature of a supplement to the original. In addition to containing some additional data concerning equiplanation, two companion terms "applanation," and "deplanation" are also suggested in the hope of presenting in a more definite and comprehensive manner certain points concerning the various plain-forming processes and the more important forces and agents they involve. It is, of course, not anticipated that these names will prove of the same importance as those above mentioned, but it is hoped that they also may serve a useful purpose.

In the preparation of this paper, the writer has been very kindly advised by Professor Isaiah Bowman of Yale University, to whom he wishes to express his sincere gratitude.

Definitions of Terms.

Before defining deplanation and applanation, it is thought advisable again to define equiplanation, in order that the relative significance of the three companion terms may be the more apparent.

Equiplanation (L. *aequus*, equal; L. *planus*, a plain) includes all physiographic processes which tend to reduce the relief of a region and so cause the topography eventually to become more and more plain-like in contour, without involving any loss or gain of material, i. e., the amounts of material

* Salisbury, R. D., "Three new physiographic terms," Jour. of Geol., vol. xii, 1904, pp. 707-715.

† Andersson, J. G., "Solifluction—a component of subaerial denudation," Jour. of Geology, vol. xiv, 1906, pp. 91-112.

‡ The title of the paper read was: "Differential erosion and equiplanation in portions of Yukon and Alaska."

remain apparently equal, or are not increased or decreased by the plain-producing process or processes. Material may be exported from certain districts during the time equiplanation is in progress, but this export takes place quite independent of the equiplanating.

Deplanation (L. *de*, from ; L. *planus*, a plain) includes all physiographic processes which tend to reduce the relief of a district, and so cause the topography eventually to become more and more plain-like in contour, dominantly by subtracting material from the area or areas affected.

Applanation (L. *ad* to or upon ; L. *planus*, a plain) includes all physiographic processes which tend to produce land-forms having plain-like surfaces, or tend to reduce the relief of a district and so cause the topography eventually to become more and more plain-like in contour, dominantly by adding material to the area or areas affected.

Classification of Physiographic Processes.

All physiographic processes, forces, or agencies that tend to alter the topography of a district by reducing the relief and so eventually cause the surface to become more plain-like in contour, may thus be considered as deplanating, applanating, or equiplanating in character, depending upon whether their activities result dominantly in a loss, a gain, or neither loss nor gain, respectively, of material, within the areas affected. Many processes or forces, however, such as certain forms of volcanic activity and some phases of diastrophism, instead of producing plain-like surfaces, tend primarily to destroy them. All physiographic processes that do not tend ultimately to reduce the relief of the region in which they are engaged, may thus be regarded as "nonplanating." It is thought that it may be conducive to a clearer understanding of various physiographic processes, if each be considered under the division of this suggested classification to which it belongs. Normal stream action, for instance, has a deplanating effect, but in districts having interior drainage, the results of stream action are to produce equiplanation. Similarly, wind action may be either deplanating, applanating, or equiplanating. Frost action may be strongly deplanating in character, or may be an important factor in causing equiplanation.

Most modern writers in describing plain-like surfaces, which here include both plains and plateaus, consider these all to belong to one of two main genetic types. For example, Geikie* classifies plains as :

* Geikie, James, "Earth sculpture," pp. 335-339, 1898.

1. Plains of accumulation.
2. Plains of erosion.

Other writers divide plains into:

1. Peneplains.
2. Constructional plains.

These are typical of the various modern classifications of plain-like surfaces where such are based upon genesis. Many writers thus appear to consider that plain-like surfaces are produced entirely either by erosion or deposition, i. e. by either subtraction of material from or addition of material to the areas affected, that is by deplanation or applanation. No credit is given to equiplanating processes, although these, especially in desert countries, have frequently been described. In such regions, the eroding or abrasive forces have been quite as effective as those of deposition.

Equiplanation.

In the writer's original paper dealing with equiplanation, this term is defined and the process is considered in a general way. Also a special phase of equiplanation that was found to be active in portions of Yukon and Alaska is also described.

In portions of the Yukon plateau which is generally considered to represent an uplifted and subsequently dissected peneplaned surface,* extensive portions of but gently undulating upland from 3,000 to 3,500 feet above sea-level are still preserved that are now dissected by deep, steep-walled, depressions representing the main drainage-ways of the areas. On the upland, forces are engaged in dissolving and disintegrating the rock material constituting the residuals or monadnocks, and are transporting this to the intervening depressions, where it is deposited. On account of the arctic climate there prevailing, the material, wherever deposited, is soon frozen or becomes associated with other frozen debris, and is consequently held, and added to the flat or nearly flat surface accumulations of superficial deposits which extend over considerable portions of the plateau that are but very imperfectly drained on account of the perpetual frost in the ground. In this way the bedrock depressions of the upland are becoming filled with material derived from the adjoining higher elevations. Thus, the

* Dawson, G. M., *Trans. Roy. Soc. of Can.*, vol. viii, sec. 4, 1890, p. 13. Brooks, A. H., "Geography and geology of Alaska," *U. S. Geol. Surv.*, 1906, Prof. Paper, No. 45, pp. 36-41, 288-290. Spurr, J. E., "Geology of Yukon gold district, Alaska," *Eighteenth Ann. Rep. U. S. Geol. Surv.*, Pt. III, 1898, p. 260. Spencer, Arthur C., "Pacific mountain system in British Columbia and Alaska," *Bull. Geol. Soc. of Am.*, vol. xiv, pp. 117-132, 1903. Hayes, C. E., "Expedition through the Yukon district," *Nat. Geog. Mag.*, vol. iv, p. 129, 1898.

tendency is for this elevated surface to become gradually more and more plain-like in contour, without experiencing any regional loss or gain of material.

A prolonged rise of temperature, however, would thaw the accumulations of debris on the upland, and would result in the greater amount, at least, of this material being rapidly removed by water action to the main valleys.

While equiplanation is engaged in planating the upland, normal erosion is slowly destroying the remaining portions of

FIG. 1.



FIG. 1. General view of the dissected upland surface of the Yukon plateau along the 141st meridian (the Yukon-Alaska International boundary) at north latitude $66^{\circ} 50'$. This upland has an average elevation of about 3,500 feet above sea-level.

this surface by more completely dissecting it, and by widening the intersecting drainage depressions and causing the valley-walls of neighboring streams to gradually approach one another.

The equiplanating process here described is not thought to be limited to the particular district under consideration, but is believed to be more or less active throughout extensive areas subjected to an arctic climate. Since, however, these areas have been but little explored, the phenomenon has not been described.

In regions having interior drainage, equiplanation is also nearly everywhere in evidence. There, wind action, stream and water action, and the various other subaërial destructive and constructive physiographic forces, slowly diminish the relief by constantly removing material from the higher, generally peripheral areas, and depositing it on the basin floors of the various centripetal systems, thus causing all the local base-levels to rise. This is a true equiplanating process, as by it the relief is reduced and the surface of each region so affected tends to become more and more plain-like in contour, and in so

FIG. 2.



FIG. 2. A view of the upland surface, 3,500 feet above sea-level, along the 141st meridian (the Yukon-Alaska International boundary) at north latitude $66^{\circ} 51'$. Equiplanation is here active; the material composing the abrupt-edged limestone residual is being disintegrated and dissolved and subsequently added to the accumulations of debris that fill the adjoining bed-rock depressions.

doing no loss or gain of material is involved. In many such regions having interior drainage, however, more or less fine material is exported by the wind, as explained under "deplanation," causing the general level to become reduced. The gradational agents are, nevertheless, truly equiplanating and operate, to a large extent, independently of the deplanating wind action.

Equiplanation is particularly effective, in regions having

interior drainage, during the early stages of the physiographic cycle and under conditions just sufficiently arid to prevent the streams from reaching the sea. As the climate becomes increasingly arid, and in arid regions that are approaching a late mature or old stage in the physiographic development, more and more fine material tends to be exported by the wind. However, in many regions possessing interior drainage, the exportation of wind-borne dust is but a minor process, and equiplanation dominates the situation. Passarge has described various such districts, notable among which are certain regions such as the Kordofan type of desert, of which the climate has

FIG. 3.



FIG. 3. A view of the Yukon plateau 3500 feet above sea level, along the Yukon-Alaska boundary, at latitude $66^{\circ} 51'$. Equiplanation is active; the flat plain-like portion of the upland which here supports a typical arctic vegetation and is underlain by partly frozen accumulations of debris, is distinctly seen to be encroaching on the limestone residual bluff in the right hand portion of the picture.

recently become modified and is now somewhat more humid than formerly. In Kordofan and similar regions the rainfall is now great enough to give rise to a steppe vegetation, but is not sufficient to allow the rivers to reach the sea. Washed deposits spread over the lowlands, being coarsest about the prominent residuals, and finest in the swampy areas between the residuals, where a dark rich soil occurs.

The process of equiplanation in regions having interior drainage has been described (without specific use of the term here proposed) by Walther,* Passarge,† Penck,‡, Davis,§ and practically all recent writers of note who have dealt with desert lands. Professor Davis|| writes: "There is no novelty in the idea that a mountainous region of interior drainage may be reduced to a plain by the double process of wearing down the ranges and filling up the basins, and that the plain thus formed, consisting partly of worn-down rock and partly built-up waste, will not stand in any definite relation to the general base-level of the ocean surface."

As deserts commonly have interior drainage, and since the arid deserts of the globe, according to Sir John Murray,¶ cover over a fifth of its land surface, the vast importance of this process can be readily appreciated.

Equiplanation is thus mainly active in regions subjected to an arctic or an arid or semi-arid climate. However, nivation or snow-drift action has been noted to have an equiplanating effect in other localities. Matthes** has shown that in the Bighorn mountains, nivation tones down the features of the upland by the production of great quantities of mud which tends to fill the depressions in this surface. During seasons when the snow on the upland surface is reduced to occasional drifts, the ground in front of the drifts is kept continually moist by melting of the snow in the daytime. The water penetrates into every crevice of the underlying rock which becomes much broken and comminuted at night or on colder days when the water freezes. This excessive frost action about the receding margins of the drifts during certain seasons of the year produces a great amount of fine material which is carried away by the innumerable rills of water trickling from the edge of the snow, and lodges in the nearest slight depression.

In northern British Columbia†† and southern Yukon,‡‡ the

* Walther, J., "Das Gesetz der Wüstenbildung," Berlin, 1900.

† Passarge, E., "Die Kalahari," Berlin, 1904.

‡ Penck, A., "Einfluss des Klimas auf die Gestalt der Erdoberfläche," 1888.

§ Davis, "The geographic cycle in an arid climate," Jour. of Geol., July-Aug., 1905.

|| Davis, W. M., "Geographical essays," p. 304.

¶ Murray, Sir John, "Origin and character of the Sahara"; Science, vol. xvi, 1890, p. 106.

** Matthes, F. E., "Glacial sculpture of the Bighorn Mts., Wyo.," Twenty-first Ann. Rep., U. S. Geol. Surv., Pt. II, 1899, pp. 173-190.

†† Cairnes, D. D., "Portions of Atlin district, B. C.," Sum. Rep., Geol. Surv. Dept. of Mines, Can., 1910, p. 29; idem., "Atlin Mining district, B. C.," Memoir Geol. Surv., Dept. of Mines, Can. (in press.)

‡‡ "Wheaton River district, Yukon," Memoir Geol. Surv., Dept. of Mines, Can. (in press.)

writer has found this process to be quite active in places on the upland surface of the Yukon plateau province. This process is facilitated in Yukon by the conditions of almost perpetual frost, with the result that the fine material that collects is but slightly disturbed by running water. This process grades into that described previously as being effective in other portions of Yukon and Alaska, and differs from it largely in that, to the south, nivation has acted in conjunction with other disintegrating and dissolving agencies. To the north, however, the process is really the more effective and is more truly equiplanating in character, as practically no material escapes from the upland areas of accumulation, whereas to the south the climate is less rigorous and running water is an eroding and transporting factor even on the plateau surface.

Although snow-drifts have this tendency to reduce the relief in gently undulating upland areas, they have a tendency to accentuate the topographic features when the snow gathers along valley walls and on steep slopes. The drifts excavate year by year, increasing in size as their fostering basins are enlarged, and thus tend eventually to be transformed into ice, and to become in time the cirque heads of valley glaciers. This process has been described in a very lucid and instructive manner by Matthes.*

Equiplanation is thus a process by which levelling occurs without reference to sea-level, and is in this respect fundamentally different from peneplanation and marine planation. The surfaces affected by equiplanation in the majority of regions, however, are above sea-level, but there are districts such as the Salton sink,† north of the Gulf of California, in which the central basin is below sea-level.

Deplanation.

All topographic terranes having plain-like surfaces‡ that have been produced dominantly by deplanation, may be grouped in one of the three following categories :

1. Peneplains.
2. Plains of marine denudation.
3. Glacial plains.

The chief agents capable of producing these forms, and of assisting in deplanating processes, include land-ice, the sea, and all subaërial erosive, disintegrating, and transporting forces, in regions having exterior drainage. In regions having interior

* Matthes, F. E., "Glacial sculpture of the Bighorn Mts., Wyo.," Twenty-first Ann. Rep., U. S. Geol. Surv., Pt. II, 1899, pp. 179-190.

† Davis, A. P., "The new inland sea," Nat. Geog. Mag., Jan., 1907, pp. 37-49.

‡ This here is intended to include plateaus as well as high and low plains.

drainage, as shown previously, all physiographic agencies, including stream-action, wind, and weathering forces, have equiplanating tendencies; in addition to assisting equiplanation, by depositing over the lowlands material eroded from the surrounding and included residual highlands, the wind also exports vast amounts of fine dust to neighboring regions. In so far as the desert tracts are made more plain-like by the removal of exported, wind-borne material, this process is deplanating, and may become effective in the mature and old stages of an arid cycle. However, instead of smoothing the surfaces of desert lands, the wind more frequently has a roughening effect. So extensive, in fact, is this process that the drainage which, during the late mature stage of an arid cycle, tends to be reduced to a completely integrated condition, becomes during the later stages again disintegrated largely by the production of wind-blown hollows. The plain-producing forces in regions having interior drainage are thus regarded as being dominantly equiplanating in character. In areas having exterior drainage, the wind is a true deplanating agent and produces its quota of fines, which is added to that resulting from the other destructive physiographic agencies, and eventually commences its stream-borne journey toward the ocean. The deplanating activities of the sea and of inland-ice are outlined in later paragraphs.

Probably much the most extensive of the surfaces produced by deplanation are those generally considered to be uplifted peneplains. Peneplains and plains of marine denudation may be readily distinguished from glacial plains or plains produced by inland-ice,* but between the first two there is greater similarity.

In certain regions, also, there is considerable uncertainty as to whether planation is due to normal erosion (peneplanation) or was produced during an arid climate and under interior drainage conditions, and hence without reference to sea-level. It is difficult to prove, for instance, that the streams traversing the Arizona plateau had exterior drainage, during the time the region was being planated, and until this can be demonstrated, the elevation of this tract during the time of the denudation must remain uncertain.

It would, therefore, seem convenient to employ the term deplanation to include all processes, forces, agents, etc., which tend to reduce the relief of any region in which they are active, by the removal of material therefrom, regardless as to the nature or ultimate result of these activities.

* The term inland-ice is here employed to include ice-sheets or continental glaciers as contrasted with mountain or valley glaciers. See:—Hobbs, W. H., "Characteristics of existing glaciers," 1911, pp. 97, 98.

The region traversed by the Rio Grande river furnishes, perhaps, the best example known of the balance between desert and humid conditions. The stream is just powerful enough to overflow from one basin to another and escape to the sea, but it is not strong enough to open up a wide continuous valley.* Since this stream does get to the sea and carries some sediment, it is to this extent deplanating, but in case it were unable to do so, its activities would be entirely equiplanating.

Certain regions that are regarded as uplifted peneplains have, since their uplift, been invaded by inland or continental ice, and consequently glacial plains are there superimposed on peneplains. The region north of the Great Lakes in Canada exemplifies this phenomenon;† and vast quantities of material thought to have been removed by the ice from the surface of this territory now constitute the drift areas, till plains, moraines, etc., to the south.

Applanation.

The material added to a district in the process of applanation may be either sedimentary or igneous, and may be water-laid, wind-blown, glacial, or volcanic in character.

The sediments everywhere being carried by streams to the sea are deposited within a limited distance of the coast, and tend in time to so accumulate as to rise above the surface of the water; and at times, a relative lowering of the sea assists in this land-forming process. The coastal plain of the eastern United States is a well-known example of such a surface developed by aggradation and diastrophism. Similar processes are widespread in their operation on the earth's surface. Where the uplift is such that the beds remain horizontal, or nearly so, typical constructional sedimentary plains or applanated surfaces result. Vast accumulations of chemical precipitates, as well as the calcareous and siliceous tests of invertebrates, also are raised above sea-level in places and constitute applanated land surfaces. Sedimentation and diastrophism are thus probably the most important agents producing applanation.

Wind action, in addition to being a powerful equiplanating and deplanating agent, as described in preceding paragraphs, has also important applanating activities. Recent studies of

* Hill, R. T., "The physical geography of Texas."

† Wilson, A. W. G., "The Laurentian peneplain," *Jour. of Geol.*, vol. ii, 1903, pp. 611-669. "Physiography of the Archæan areas of Canada," *Int. Geog. Congress, Eighth Rep.*, 1905, pp. 116-135. Bowman, Isaiah, "Physiography of the United States," in *Forest Physiography*, 1911, see pp. 554-568. Martin, Lawrence, "Physical geography of the Lake Superior region," *U. S. Geol. Surv.*, Mon. lli, 1911, pp. 85-112.

the various desert areas of the world by Walther,* Passarge,* Penck,* Davis,* and many others have shown that it is by the slow process of exportation of fine wind-blown material that the mean altitudes of arid regions are continually decreased. These vast quantities of transported fines thus assist in applanating the surfaces of the adjoining regions upon which they fall; and in certain countries the accumulations of these deposits acquire very considerable thicknesses, as in the case of the loess of China or of the central plains of the United States. This wind-borne dust has frequently been shown to have been transported almost incredible distances from the arid or semi-arid districts from which it was derived. It is well known that the sails of vessels of the Atlantic to the leeward of the Sahara commonly become tinged with red, owing to the wind-blown dust from the desert; and sand grains are dredged with the true pelagic material from the bottom of this portion of the Atlantic.

Glaciation by inland-ice has also contributed vast amounts of material in places, to form drift or till plains. This also constitutes a true applanating process. Extensive plain-like areas occur on this continent just south of the 49th parallel, the surfaces of which are composed of materials that owe their origin to the continental glaciers that advanced from the north. These materials are not always so deposited as to have even, horizontal surfaces; in fact, their deposition, in places, has had a decided roughening effect on the topography. Nevertheless, extensive accumulations of drift tend to produce, in a general way, a plain-like topography, much more plain-like, in places, than the underlying bedrock surface.†

Vulcanism is also an important applanating process, and throughout extensive tracts in different countries, lavas, scoria, ashes, etc., have almost, or quite, obscured the pre-existing land surface, and have produced typical volcanic plains or plateaus. Probably the greatest lava fields in the world occur in the Columbia Plateaus of the western United States.‡ There, a region previously possessing a topography of considerable relief was subjected to successive lava flows until only the higher summits were left projecting through the volcanic

* See references to writings by these authors on a preceding page.

† Bowman, Isaiah, "Physiography of the United States," in *Forest Physiography*, 1911, pp. 460-477. Martin, Lawrence, "Physical geography of the Lake Superior region," *U. S. Geol. Surv., Mon. lli*, 1911, pp. 85-112. Carman, J. E., "The Mississippi valley between Savanna and Davenport," *Ill. State Geol. Surv., Bull. No. 18*, 1909, pp. 31-55.

‡ Russell, I. C., "A reconnaissance of Southern Washington," *W. S. & Irr. paper*, No. 4, *U. S. Geol. Surv.*, 1897. Smith, G. O., "Ellensburg folio," No. 86, 1903, *U. S. Geol. Surv.*; "Geology and physiography of Central Washington," *U. S. Geol. Surv., Prof. Paper*, No. 19, 1903, pp. 9-38.

materials. In other districts, ashes and breccia, at times accompanied by lava, have been added to surfaces in sufficient amounts to fill many of the valleys and depressions, and thus greatly reduce the topographic relief.

Conclusion.

In the foregoing paragraphs the writer has suggested certain new physiographic terms and has defined their intended significance. No attempt has been made, however, in this short paper, either to write detailed descriptions of the equiplanating, deplanating, and applanating processes, or to outline the geographical extent of their present and past activities. Volumes might be written without exhausting these subjects which include a great portion of the entire science of physiography, so that only what are thought to be some of the fundamental points and several principles concerning these processes are here briefly considered. Even to enumerate and summarily describe all the forces and agencies that contribute to equiplanation, deplanation, and applanation, and to delineate even all the most important areas in the world, where they are, or have been, in operation, would cause this paper to assume proportions far beyond what is necessary.

Moreover, it has not been the writer's purpose to attempt an interpretation of the various land-forms which might be considered; and further, there is frequently a considerable diversity of opinion among physiographers as to the origin of the various features of many well-known regions, so that in case any of these areas happened to be cited as illustrating the results of certain processes here described, a misunderstanding might arise as to the intended significance of the new terms here suggested.

It has thus seemed best merely to introduce the new terms in relation to physiographic processes, and to offer a few suggestions as to their usefulness and adaptability, and leave to others their further application and development.

SCIENTIFIC INTELLIGENCE.

I. CHEMISTRY AND PHYSICS.

1. *The Higher Layers of the Atmosphere.*—ALFRED WEGENER has given an interesting discussion of this subject, upholding the view that there are higher strata of the earth's atmosphere of entirely different composition from that of the lower atmosphere. As long ago as 1875 Hann concluded from a theoretical consideration of the laws of gases that the upper atmosphere must consist of pure hydrogen, if this gas, as supposed, was a constituent of the air. In 1903, after the work of Gautier had indicated the probable presence of a minute quantity of hydrogen in the air, Hann made further calculations and reached the conclusion that at a height of 50 km. the air would contain 14 per cent by volume of hydrogen, while at 100 km. there would be 99 per cent of it. Somewhat later Wegener expressed the view that at a height of 70–80 km. there must be a sudden change in density of the atmosphere for the reason that Krakatoa clouds stopped at this height, and that this is the limit at which diffuse reflection of light is observed. Afterwards he made calculations similar to Hann's and found, by using smaller intervals of height, that there was theoretically a sudden change in composition at exactly the same altitude at which he was led to assume a limiting layer for other reasons. He called attention to the analogy between such a sharply limited hydrogen atmosphere, surrounding the earth, to the well-known hydrogen atmosphere of the sun's chromosphere, and he advanced the view that above the hydrogen layer there might be found another stratum of a still lighter gas corresponding to the coronium of the sun. This supposition of a higher layer is based upon the position of the highest northern lights, which like coronium give a green spectrum line, although these lines are different.

Another argument in favor of a distinct, higher stratum of the atmosphere has been brought forward in connection with the highly remarkable sound phenomena that occurred in connection with the great dynamite explosion at the Jungfrau railroad on November 15th, 1908. There was a normal region of audibility extending about 40 km. and immediately surrounding the place of explosion; then there was a second, abnormal, and much more extensive, region of sound, which was separated from the first region by a "zone of silence" about 100 km. wide. While this phenomenon was at first attributed to a change in wind at a high altitude, the hypothesis was advanced by v. dem Borne that it was due to a reflection of the sound-waves upon the higher hydrogen layer of the atmosphere, and his calculations showed that this view was very plausible in connection with the facts of the case.

From a consideration of observations upon the appearance of twilight the height of the upper limit of the atmospheric layer reflecting light is placed at about 74 km. After this "end of twilight" there is, however, a very pale, bluish light, the observation of which led See to estimate the height of the corresponding reflecting layers at 214 km. Wegener believes it probable that this altitude corresponds to the boundary between the spheres of hydrogen and the hypothetical lighter gas, which he calls "geocoronium."

Since observations show that small meteors begin to glow at a height of about 150 km. and go out at about 80 km., it appears that their play is entirely within the hydrogen atmosphere, if the conclusions here advocated are true. In that case their luminosity is due to their collision with hydrogen, and their disappearance is probably caused by volatilization. Larger meteors often show a great increase in brilliancy at a certain point in their course, thus indicating a sudden change in the atmosphere, and they have been observed to explode at heights varying from 3·7 to 46·7 km.

It is important in this connection that Pickering found several hydrogen lines in the spectrum of the luminous trail of a meteor, although Blajko in two cases observed very bright lines at 393 and 389, which Wegener takes to be identical with the nitrogen line 391, which is very prominent in northern light spectrum, and hence he believes that these meteors had penetrated to the nitrogen atmosphere.

The amount of oxygen in the air has been found to vary but little, or not at all, from the surface of the earth to an altitude of 15½ km. This is attributed to vertical mixing, but an analysis of air from a height of 8 km. by E. Erdmann showed per liter a total of 37·7^{cc} of helium, neon and hydrogen, the lightest constituents of the air, while air at the surface of the earth contains 26·2^{cc} of these gases. Similar results were obtained by Hugo Erdmann by the comparison of air from the surface with that from an altitude of 4 to 4½ km., so that it appears that in spite of vertical mixing, a concentration of the lighter constituents with the altitude is indicated.

Several arguments, based upon the appearance and spectra of the aurora borealis, are brought forward in favor of the layer theory of the atmosphere, but they will not be noticed in detail here. It should be mentioned, however, that Scheiner has expressed the opinion that the northern light lines indicate the presence of an unknown, very light gas, and the author takes occasion to identify this with Mendeléeff's speculative element with the atomic weight 0·4, and with his own hypothetical "geocoronium," which he believes to form a stratum above the hydrogen stratum.

The following tables give the results of the author's calculations where the hypothetical geocoronium is taken into account :

Composition of the Air at the Earth's Surface.

	Mol. wt.	Volume percentage.
Geocoronium, (monatomic) ...	abt. 0.4	abt. 0.00058 (hypothetical)
Hydrogen, H ₂	2.02	0.0033 (Gautier, Rayleigh)
Helium, He	4.0	0.0005 (Claude)
Water, H ₂ O	18.02	0-4, variable
Neon, Ne	20.0	0.0015 (Claude)
Nitrogen, N ₂	28.02	78.06 (Ledue)
Oxygen, O ₂	32.00	20.90
Argon, Ar	39.9	0.937
Carbon dioxide, CO ₂	44.0	0.029, variable
Ozone, O ₃	48.0	Traces (Thierry)
Krypton, Kr	83.0	abt. 0.0001
Xenon, X	130.7	abt. 0.000005

Composition of the atmosphere in volume-percentage.

Altitude km	Pressure mm	(Geo- coronium)	Hydro- gen	Helium	Nitro- gen	Oxygen	Argon
0	760	0.00058	0.0033	0.0005	78.1	20.9	0.937
20	41.7	0	0	0	85.	15.	0
40	1.92	0	1	0	88	10.	—
60	0.106	5	12	1	77	6	—
90	0.0192	19	55	4	21	1	—
100	0.0128	29	67	4	1	0	—
120	0.0106	32	65	3	0	—	—
140	0.00900	36	62	2	—	—	—
200	0.00581	50	50	1	—	—	—
300	0.00329	71	29	—	—	—	—
400	0.00220	85	15	—	—	—	—
500	0.00162	93	7	—	—	—	—

The author claims only roughly relative values for the quantities given in the second table.—*Zeitschr. anorgan. Chem.*, lxxv, 107.

H. L. W.

2. *Allen's Commercial Organic Analysis*. Vol. VI, Fourth Edition, Entirely Rewritten. Edited by W. A. DAVIS and SAMUEL S. SADTLER. 8vo, pp. 726. Philadelphia, 1912 (P. Blakiston's Son & Co.).—This volume deals with the organic bases, and includes the following sections: Amines and ammonium bases; Other bases from tar; Vegetable alkaloids; Volatile bases of vegetable origin; Nicotine and tobacco; Aconite alkaloids; Atrophine and its allies; Cocaine; Opium alkaloids; Strychnos alkaloids; Chinchona alkaloids; Berberine and its associates; Caffeine, tea and coffee; Cocoa and chocolate. As nearly twenty years have elapsed since the last edition of this volume was issued, very far-reaching alterations have been necessary in its revision. The book will be very useful to those interested in this branch of analytical chemistry.

H. L. W.

3. *Methods for Sugar Analysis and Allied Determinations*; by ARTHUR GIVEN. 8vo, pp. 75. Philadelphia, 1912 (P. Blakiston's Son & Co.).—This is a valuable compilation of those methods used for the analysis of sugars and similar materials which the author has found from practical experience to be most useful and accurate. Methods are given for the analyses required for the control of cane and beet sugar manufacture; for the examination of maple products, honey, glucose and sugars in various food products; and for dextrin and starch. There are several illustrations of special forms of apparatus and a number of valuable tables.

It would seem that the avowed intention of the author to make plain the way for the inexperienced might have been well served by a few pages of general introductory matter setting forth the principles of sugar analysis; the opening paragraphs seem like a rather cold plunge for an inexperienced analyst. The book especially commends itself by giving straightforward directions for the analysis of each material, avoiding a confusing array of alternate methods.

A. L. D.

4. *Laboratory Exercises in Physical Chemistry*; by J. N. PRING. 12mo, pp. 162. Univ. of Manchester Publications (Longmans, Green & Co.), 1911.—This book gives excellent directions for the usual determinations and there is enough theory included to make the object of the experiments clear. It is possibly a little one-sided, as more than half is devoted to electrochemistry and electrolytic experiments. Since physico-chemical measurements are usually carried on only by somewhat advanced students, it would be an advantage to have more references to the original literature than are given.

H. W. F.

5. *Die Entdeckung des Radiums*; by Mme. CURIE. Pp. 28, with 5 figures. Leipzig, 1912 (Akademische Verlagsgesellschaft m. b. H.).—This pamphlet is the authorized German edition of the address made in Stockholm on December 11, 1911, by Marie Curie on the occasion of the presentation to her of the Nobel prize for chemistry. The paper deals primarily with the history of the discovery of radium and with the importance to chemistry of the final isolation of radium in the elementary form.

H. S. U.

6. *Über neuere thermodynamische Theorien (Nernstsches Wärmetheorem und Quantenhypothese)*; by Dr. MAX PLANCK. Pp. 34. Leipzig, 1912 (Akademische Verlagsgesellschaft m. b. H.).—This is a formal reproduction of a lecture delivered, on December 16, 1911, before the German Chemical Society. For details suggested by the parenthetical title reference must be made to the original article.

H. S. U.

7. *Studies in Terrestrial Magnetism*; by C. CHREE. Pp. xii, 206, with 43 figures and 74 tables. London, 1912 (Macmillan and Co., Ltd.).—The object of this book is made very clear by the author, who says:—"The volume does not aim at being a text-book of Terrestrial Magnetism, or at summarising existing

knowledge in those branches of Terrestrial Magnetism with which it deals, but is intended to give a connected account of my own original work in that subject, referring to the work of others only so far as is necessary for intelligibility." Some of the subjects dealt with are the following :—magnetic records, secular and non-cyclic changes, diurnal inequalities, annual variations, comparison of arctic and antarctic disturbances, sunspots and terrestrial magnetism, etc.

H. S. U.

8. *A Physical Study of the Firefly*; by WILLIAM W. COBLENTZ. Pp. 47, with 14 figures and 1 plate. Washington, 1912 (Publication No. 164 of the Carnegie Institution of Washington).—This paper gives the results obtained by a systematic investigation, extending over a period of about four years, of the light emitted by various organisms, especially by the fireflies *Photinus pyralis* and *Photuris pennsylvanica*. Careful and accurate determinations have been made of the spectral energy curves of the light emitted by fireflies, of the luminous efficiency and candle-power, of the radiations and temperature, and of the infra-red absorption. The spectrograms reproduced on the plate are clear-cut, and the whole subject is presented in a thorough and interesting manner. At the end of the paper may be found a bibliographical list of the most important articles bearing on the subject.

H. S. U.

9. *Elements of Hydrostatics*; by GEORGE W. PARKER. Pp. viii, 150, with 48 figures. London, 1912 (Longmans, Green & Co.).—This book is intended to be a sequel to the author's "Elements of Mechanics." The treatment is very elementary, and presupposes only an acquaintance with algebra, geometry, and a few fundamental principles of mechanics. Numerous illustrative problems are worked out in the text, and 204 examples for solution by the student are collected in 16 sets. The answers to these original problems are given at the end of the volume. The author lays stress on the importance of solving problems directly from basic principles, and discountenances the substitution of numerical data in algebraic formulæ, whenever this process can be reasonably avoided.

H. S. U.

II. GEOLOGY AND NATURAL HISTORY.

1. *The Effect of Topography and Isostatic Compensation upon the Intensity of Gravity*; by JOHN T. HAYFORD and WILLIAM BOWIE. U. S. Coast and Geodetic Survey. Pp. 132; 19 illustrations. Washington, D. C., 1912.—It has long been known that the larger topographic provinces of the earth's surface hold their different vertical relations because of different densities in the subcrust, the solid crust thus resting in equilibrium; but it remained for Hayford to show that the relation was very close, areas as small as ten thousand square miles commonly having their mean elevation as much as nine-tenths compensated. He

showed further that the variations in density which are expressed by the surface relief occur within a hundred miles of the surface; the most probable value, on the assumption that the compensation is complete and uniformly distributed, being seventy-six miles. This conclusion enabled the influence to be computed of these variations of density upon the intensity of gravity at the earth's surface. The present work embraces the results of such an investigation, utilizing 89 stations in the United States and 16 selected stations not in the United States. For each station the whole earth's surface was divided into 317 compartments. Then the influence of the topography and the corresponding subsurface density, on the assumption of complete compensation, was computed for each compartment. The outstanding difference between the computed and observed values of gravity are known as the "new method anomalies" and are much smaller than the anomalies computed by previous methods. Thus the results confirm and supplement those of the studies on the deflection of the plumb-line. Together the two kinds of evidence locate ten areas within the United States of excess or deficiency of subsurface mass with reasonable certainty (see plate 19). There is little hope, however, of determining by the use of gravity observations the manner of the distribution of the isostatic compensation with regard to depth.

J. B.

2. *New Zealand Department of Mines, Geological Survey Branch*; P. G. MORGAN, Director. *Bulletin No. 18 (New Ser.), The Geology of the Greymouth Subdivision, North Westland*; by PERCY GATES MORGAN. Pp. viii, 159; with 6 plates, 9 diagrams, 8 maps, 3 geological sections. Wellington, 1911.—The fact that half of the population of Greymouth is engaged in gold and coal (Eocene) mining justifies the extensive treatment of these industries in a geologic report of that district (pp. 15–30, 82–150). The area includes, however, much of interest in addition to its economic development. The description of an ancient coastal plain (upper Miocene in age), built of river gravels and glacial debris as well as of marine clays and sandstones and marked by raised beaches, furnishes additional data on a complex physiographic feature which appears to be coextensive with the Islands. The entire district has been glaciated and presents typical lakes and moraine deposits. The geological column includes argillites of Paleozoic (period undetermined) age, sediments of Eocene, Miocene, Pliocene, and Pleistocene periods, with intrusive basic and granitic masses of pre-Tertiary age. During the Paleozoic and Mesozoic the island "was part of or adjoined a continental area," and an extensive uplift at the close of the Mesozoic gave New Zealand continental dimensions. The author of the Greymouth report succeeds Dr. Bell as Director of the New Zealand Geological Survey, and it is gratifying to note that the high standard of scientific work, as well as the excellence of published maps and reports, set by the Survey is to be maintained.

H. E. G.

3. *Physical Geography for South African Schools*; by ALEX. L. DU TOIT. Pp. xii, 250; map, 68 figures. Cambridge, 1912 (The University Press).—Mr. DuToit's little volume possesses the characteristics of a satisfactory text-book in concise statement, ample verbal and pictorial illustrations, and pleasing appearance. To those interested in South Africa the book will be very acceptable, for without it the physiographic data of this interesting region must be gathered from technical and general reports. The physiographic map of South Africa (bound with the book), constructed from all available data, is a particularly valuable contribution.

H. E. G.

4. *Notes on fossils from limestone of Steeprock Lake, Ontario*; by CHARLES D. WALCOTT. Mem. No. 28, Geological Survey Canada, Appendix, 6 pages, 2 plates, 1912.—In this short paper is announced the remarkable discovery of "organisms related to the sponges, or possibly to forms possessing characters of both the sponges and *Archæocyathinæ*" found by Lawson in 1911 at the base of the *Lower Huronian*, in the Steeprock limestones north west of Atikokan, Ontario, on the Canadian Northern railway. Walcott says, "The *Archæocyathinæ* are of late lower Cambrian age, and if the stratigraphic position were not well determined I should be inclined to consider *Atikokania* [new genus] as a lower Cambrian genus." These cone-shaped, thick-walled fossils with a small central and apparently open cavity, attain a diameter of at least two inches. The two new species are *A. lawsoni* and *A. irregularis*.

C. S.

5. *A report on some recent collections of fossil Coleoptera from the Miocene shales of Florissant*. Bull. State Univ. Iowa, Vol. vi, No. 3, pp. 3-38, pls. i-vi, 1912. *On some fossil rhynchophorous Coleoptera from Florissant, Colorado*. Bull. Amer. Mus. Nat. Hist., Vol. xxxi, Art. iv, pp. 41-55, pls. i-iv, 1912.—Two interesting papers by Professor H. F. WICKHAM on beetles from the lake deposits of Miocene age occurring about Florissant, Colorado. It is the author's intention to describe all of the beetles from this most interesting locality. The Rhynchophora are a dominant type of beetles in Miocene time. The author sees no direct relationship between the Florissant forms and those of Central America, as noted by Scudder, but finds the affinities to be with those of the United States.

C. S.

6. *Glacial Man in England*.—The Geological Magazine for April (Vol. IX, No. IV), 1912, contains two articles of interest in connection with the reported finding of a human skeleton in the glacial deposits of Ipswich. GEORGE SLATER (Occurrence of a Human Skeleton in Glacial Deposits at Ipswich, pp. 164-168) examines the geological evidence, discussing the observations and interpretation of Mr. Moir, Mr. Whitaker, Dr. Marr, and Professor Keith. The conclusion is reached:

"The evidence as to the position of the bones seems to be unmistakable; they were found partly in the Boulder-clay and partly in the sand. It is difficult to understand how this could

have occurred naturally under any circumstances. The sand was presumably deposited by running water, the Boulder-clay by moving ice, entirely different conditions obtaining at different times."

"All the evidence points to the probability that the man was buried in a narrow, shallow grave, but there is no evidence as to when this took place; we can only label the skeleton 'of doubtful age'."

Professor T. McKENNY HUGHES calls attention (pp. 187-188) to the relative rapidity with which traces of interment are obliterated.

H. E. G.

7. *Geological and Natural History Survey of Connecticut*; WILLIAM NORTH RICE, Superintendent. Bulletin, No. 18, Triassic Fishes of Connecticut; by CHARLES R. EASTMAN. Pp. 77; 11 plates, 8 text figures. The appearance of this important bulletin has already been announced in this Journal. (See Lull, vol. xxxiii, p. 399.)

8. *Report on the Progress and Condition of the Illinois State Museum of Natural History 1909-1910*; by A. R. CROOK, Curator. Pp. 557.—This volume gives an account of the recent growth of the Illinois State Museum, with the additions to the collections both by purchase and gift; a catalogue of the Museum library and a list of fossils on exhibition are also included. The Museum has been fortunate in the number of gifts received, showing the wide interest of the people of the state in these collections; under the circumstances it would seem as if a more liberal state allowance for Museum expenses might well be made. The total amount granted for the two years closing with July 1, 1911, was only \$6,450 per annum; it is remarkable that so much has been accomplished with this scanty income.

9. *Mineralien-Sammlungen. Ein Hand- und Hilfsbuch für Anlage und Instandhaltung mineralogischer Sammlungen*: von Dr. WOLFGANG BRENDLER. II Teil. Pp. viii, 699. Leipzig, 1912 (Wilhelm Engelmann).—The first part of this work, which is specially designed to help those concerned with the installation of mineral collections, was noticed in this Journal three years since (vol. xxvii, p. 343). The present volume gives a list of mineral species arranged according to Groth's well-known tables, with a brief statement of the composition, crystallization, and the most prominent physical characters. Then follows in each case a full and carefully prepared record of localities, geographically arranged. This part of the work is supplemented by an exhaustive index, showing what species occur at the different localities. The painstaking care given by the author to this part of his work will be appreciated from the fact that in the case of the geographical names in Greenland the meaning of each name is given in full, with a minute statement as to locality.

10. *Der Diamant: Eine Studie von A. VON FERSMANN und V. GOLDSCHMIDT*. Pp. xvii, 274; with an Atlas of 432 plates. Heidelberg, 1911 (Carl Winter's Universitätsbuchhandlung).—The authors of this handsome work have carried through a remark-

ably thorough and exhaustive study of the forms of the diamond. It is a study of peculiar interest, not only because of the value and rarity of the specimens themselves, but also because of the many peculiarities of crystalline structure which the crystals of this species exhibit. The completeness of the present work will be appreciated from the fact that 131 crystals have been examined, and besides the description in the text, the results are given in 292 figures on 42 admirable plates. Many of these plates have a thin paper cover, making possible the minute description of the forms figured. In the case of the twin crystals, many of them highly complex and extremely interesting, the figures are cleverly colored so as to exhibit the relations of the different individuals. The authors decide definitely in favor of the hemihedrism of the diamond, a point about which there has been some difference of opinion. As it is expressed, however, this hemihedrism is not always distinctly shown; or, in other words, the difference between the two tetrahedrons is often not prominent. In the case of an investigation of such thoroughness and minuteness, it would be difficult to give an idea of the contents of the volume without much detail of description, but attention is to be called to the point that the rounded surfaces of the crystal form, and the many peculiarities of the faces themselves, are treated very fully with reference to the conditions of their origin.

11. *The British Tunicata*; an unfinished monograph by the late JOSHUA ALDER and the late ALBANY HANCOCK, edited by JOHN HOPKINSON. Volume III, *Aggregatæ (Ascidia Compositæ)*. Pp. xii, 113; 16 plates, mostly colored. London, 1912 (The Ray Society).—This volume completes the excellent monograph prepared by the Secretary of the Ray Society from the unpublished drawings and manuscript left successively by Alder and Hancock at their death about thirty years ago. The two earlier volumes of the series (see this Journal, xx, 469, xxiii, 398) described the simple ascidians of the British coast, while the concluding volume treats of the compound forms. The illustrations by Alder, most of which are from colored drawings of the living animals, are supplemented by others copied in colors from Milne Edwards' well-known monograph. W. E. C.

12. *Ceylon Marine Biological Reports*, Part VI, Nos. 20 to 22; *Report on Certain Scientific Work done on the Ceylon Pearl Banks during the Year 1911*, with three plates and three charts; by T. SOUTHWELL and LIEUTENANT J. C. KERKHAM, Colombo (Government Printer), Ceylon, 1912.

This report consists of three separate papers, two of which deal with nautical notes and observations, while the third contains descriptions of ten new species of cestode parasites of the marine fishes of Ceylon.

The announcement is made that because of the failure of the pearl fisheries of the region during several recent years the laboratory is to be abandoned and no further reports issued.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *The Carnegie Foundation for the Advancement of Learning. Bulletin No. 6. Medical Education in Europe*; by ABRAHAM FLEXNER, with an Introduction by HENRY S. PRITCHETT. Pp. xx, 357. New York, 576 Fifth Avenue, 1912.—Some two years ago (see this Journal, xxx, 94) the Carnegie Foundation published a report by Dr. Abraham Flexner criticising with much frankness the unsatisfactory condition of much of the medical instruction in the United States. This report is now followed by a second publication by the same author detailing the conditions as regards instruction in this subject in foreign countries, including particularly Great Britain, Germany, France and Austria. An introduction at length is given by President Pritchett. The conclusions reached are by no means flattering to the methods employed in this country. The absence of any adequate clinical facilities in many of the medical institutions, even those situated in states where the general standard of instruction is high, is the feature that is justly most condemned. President Pritchett says:

"Scandals in medical education exist in America alone. In no foreign country is a medical school to be found whose students do not learn anatomy in the dissecting-room and disease by the study of sick people. It has remained for the United States and Canada to confer annually the degree of doctor of medicine upon, and to admit to practice, hundreds who have learned anatomy from quiz-compendes, and whose acquaintance with disease is derived not from the study of the sick, but from the study of text-books. These scandalous conditions are less widespread to-day than they were a decade ago; yet they are still to be found in almost all sections of the country, even in the most cultivated." . . .

Furthermore, as regards examinations, for example, written papers are often alone required, making it possible for a student to pass who has had neither laboratory nor clinical instruction. The development of numerous types of medical sects known by different names, which is practically unknown in Europe, is believed to be due to the fact that in America "sectarian medicine can be practised on lower terms than scientific medicine."

That the best of American medicine and surgery is on a very high plane indeed is well recognized, but this fact does not remove the evils so often present due particularly to the causes discussed at length in this report.

2. *The proposed Expedition to Crocker Land*.—It is announced by the committee in charge that the Crocker Land Expedition, which was to have started this summer under the leadership of George Borup and D. B. MacMillan, has been postponed to the summer of 1913, on account of the death of George Borup on April 28. It is proposed to carry forward the enterprise without essential change as to the main objects although some reorganiza-

tion will be necessary. The Expedition will be a memorial to George Borup, the young explorer who was so keenly interested in it and who was the mainspring of the original undertaking. Mr. MacMillan's connection with the enterprise continues as heretofore, and he is utilizing the intervening time for the purpose of making additional preparation for the scientific work. Subscriptions already made are sufficient to insure the starting of the Expedition a year hence, and a considerable part of the supplies and equipment have been prepared and will be available at that time.

3. *Expédition Antarctique Française (1903-1905) commandée par le Dr. JEAN CHARCOT. Hydrographie, Physique du Globe*; par A. MATHA, J. J. REY. Pp. vi, 619; 7 plates. Paris, 1911 (Gauthier-Villars). (Ouvrage Publié sous les auspices du Ministère de la Marine.)—Among the large number of important contributions to our knowledge of the south polar regions which have been made since the century opened, an important place belongs to the work of the French Antarctic Expedition of 1903-5, commanded by Dr. Jean Charcot. This enterprise is the more interesting since, with all the work accomplished by French explorers in other parts of the world, the polar regions, north and south, have had for them little attraction. It is noteworthy also that the Charcot Expedition was organized and carried through without calling upon the public resources, although the Government has aided in the publication of the results. The region explored was that lying to the south and southeast of Cape Horn, including particularly Graham Land and the adjacent coasts. The present quarto volume is devoted to the results of the Expedition in Hydrography and Physics, presented in a series of chapters by A. Matha and J. J. Rey. The former discusses the hydrographic conditions in detail, the tides, the chronometers, the intensity of gravity, and the density and composition of the ocean water; while the latter takes up the atmospheric electricity, meteorology and terrestrial magnetism. The numerous facts brought out are particularly important when viewed in connection with the results reached by the other expeditions, the investigations of which were carried on at widely distant points in the south polar region.

4. *Publications of the Smithsonian Institution*.—The following publications made under the auspices of the Smithsonian Institution have been received:

Birds of North and Middle America; by ROBERT RIDGWAY. Part V. Pp. xxiii, 859; 33 plates. Bulletin of the U. S. National Museum, No. 50.

Asterioidea of the North Pacific and Adjacent Waters; by WALTER K. FISHER. Part I. Phanerozoia and Spinulosa. Pp. vi, 419; 122 plates. Bulletin No. 76, U. S. Nat. Mus.

Report on the Progress and Condition of the U. S. National Museum for the year ending June 30, 1911; by RICHARD RATHBUN, Assistant Secretary, in charge of the Museum. Pp. 147.—

This report gives a good idea of the activity and effectiveness of the National Museum in research and collections. The appropriations for the Museum for the given year amounted to 526,500 dollars; of special interest is the final completion of the new building on June 20, 1911, just six years after it was started.

A Dictionary of the Biloxi and Ofo Languages, accompanied with thirty-one Biloxi Texts and numerous Biloxi Phrases; by JAMES O. DORSEY and JOHN R. SWANTON. Pp. v, 340. Bureau of American Ethnology. Bulletin 47.

5. *British Museum Catalogues*.—To the important series of catalogues based upon the collections of the British Museum of Natural History and published by the Trustees, earlier volumes of which have been repeatedly noticed in this Journal, the following additions have been recently made:

Catalogue of the Chiroptera, Second Edition; by KNUD ANDERSEN. Volume I: Megachiroptera. Pp. ci, 854; 85 illustrations.—The first edition of the catalogue of the Chiroptera in the British Museum, by G. E. Dobson, was published by the Trustees in 1878. The present exhaustive work is based not only on the largely increased Museum collections, but also on an examination of the chief collections in Europe and also that of the U. S. National Museum at Washington.

Catalogue of the Lepidoptera Phalaenæ, Volume XL. Catalogue of the Noctuidæ; by Sir GEORGE F. HAMPSON. Pp. xvii, 689; 275 figures.—This eleventh volume of the Catalogue of Moths contains the Noctuid Subfamilies *Euteliæ* (12 genera, 175 species), *Stictopterinae* (10 genera, 112 species), *Sarrothripinae* (58 genera, 330 species) and *Acontianæ* (70 genera, 324 species). Plates CLXXIV–CXCI accompany this volume.

General Index to a Hand-List of the Genera and Species of Birds. Volumes I–V. Edited by W. R. OGILVIE-GRANT. Pp. iv, 199.—The fifth and final volume of the Hand-list of Birds was completed by the author, the late Dr. Sharpe, shortly before his death in 1909. The present index volume appears as a supplement to the work and is essential to its convenient use.

A Revision of the Ichneumonidæ, based on the collections of the British Museum, with descriptions of new genera and species. Part I. Tribes Ophionides and Metopiides; by CLAUDE MORLEY. Pp. xi, 88; 1 plate.

6. *Publications of the Allegheny Observatory of the University of Pittsburgh*.—The following parts of Volume II have recently appeared:

No. 16. On the presence of a Secondary Oscillation in the Orbit of 30 H. Ursæ Majoris; by FRANK SCHLESINGER. Pp. 139–150; 3 figures.

No. 16. On the presence of a Secondary Oscillation in the Orbit of Y Ophiuchi; by STELLA UDICK. Pp. 151–154.

7. *Bref och Skrifvelsen af och till CARL VON LINNÉ*. Första Afdelningen, Del VI. Stockholm, 1912.—This latest contribution to the series of volumes containing the correspondence of

Linnæus (see vol. xxxi, p. 247) contains the contributions from Swedish sources, from C. D. Ehrenpreis to J. G. Hallman.

8. *Essais de Synthèse Scientifique*; par EUGENIO RIGNANO. Pp. xxxi, 294. Paris (Librairie Félix Alcan).—This series of essays deals with important questions in biology and sociology, involving vital matters concerning the biological basis and the nature of the tendencies affecting the conscience, the origin and evolution of religion, etc.

9. *Rationalist English Educators*; by GERALDINE E. HODGSON. Pp. 254. London, Brighton (Society for Promoting Christian Knowledge), New York (E. S. Gorham), 1912.—This volume is an important contribution to the history of education in England, a subject which, indeed, lies outside of the scope of this Journal. A chapter is devoted to the predecessors of Locke, five others to the work of Locke himself from various standpoints, and other chapters to the Edgeworths and John Stuart Mill.

10. *Zeitschrift für Gährungsphysiologie; allgemeine, landwirtschaftliche, und technische Mykologie*; herausgegeben von Professor Dr. ALEXANDER KOSSOWICZ, Wien. Band I, Heft 1, March 1912. Berlin (Gebrüder Bornträger).—In the midst of an unparalleled multiplication of scientific publications the advent of a new journal calls for some justification for its appearance. This new "Zeitschrift" is intended to bring together the rapidly growing literature on microorganisms and mycology now scattered in various chemical, agricultural, technical, botanical, and medical publications. It aims to publish original contributions as well as reviews and abstracts on systematic mycology, agricultural bacteriology, and the microbiology of the food industries, water supply and sewage. The most important paper in the current number is a review of the progress of agricultural bacteriology in 1910 and 1911 by F. Löhnis. Among the fifty collaborators on the title page the name of one American, Dr. W. A. Harding, is included.

L. B. M.

11. *Meteorology: A Text-book on the Weather, the Causes of its Changes, and Weather Forecasting*; by WILLIS I. MILHAM. Pp. xvi, 547; 157 figures, 50 charts. New York, 1912 (The Macmillan Company).—In the selection of data, use of references, acceptance of hypotheses, and in conclusions reached, Professor Milham keeps safely away from controversial matter, and has given a conventional treatment of meteorology, suitable for readers who wish to become familiar with the present state of the science. The strong points of the book are those which appeal to the teacher, viz., a logical outline worked out in detail, clear style, lists of test questions and practical exercises, and extensive, carefully chosen and classified references.

H. E. G.

12. *Chemical Research in its Bearings on National Welfare*; by EMIL FISCHER. Pp. 80. London, 1912 (The Society for Promoting Christian Knowledge).—The substance of this little volume is a lecture delivered in Berlin in January, 1910. An Introduction is added showing what Germany has accomplished in developing chemical research and calling for the establishment in England of an institution similar to the Kaiser-Wilhelm Society in Berlin.

New Circulars.

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[FOURTH SERIES.]

ART. IX.—*The Interferometry of Air Carrying Electrical Current*; by CARL BARUS.

1. *Introduction.*—The following experiments, though leading (as was to be anticipated) to negative results, are nevertheless sufficiently interesting in their details to deserve to be reported. The object in view was a direct test as to whether a rarefied column of air, through which a current of electricity is flowing, shows any perceptible change of its index of refraction. Such an effect might result from the occurrence of ionization, or from rise of temperature, or finally, in the extreme case, from a possible influence of rapidly moving corpuscles on the velocity of light traveling in the same direction as the corpuscles. The means of exhaustion at present at my disposal were not sufficient to carry the vacuum much below one millimeter of mercury; neither were exceptionally large potential differences employed, so that the experiment has not been pushed to a limit at which it might possibly show results. I shall hope to return to the work at some other time. The present paper attempts therefore to do no more than to describe the adaptability of the displacement interferometer for the present purposes.

2. *First Experiments. Apparatus.*—At the outset the interferometer was used without other modification than a marked elongation of the arms GM and GN , where G is the grating, M (the micrometer) and N the opaque mirrors. The component beams of light m and n were now one meter in length each, so that a glass tube t , hermetically sealed at its ends with plate glass windows, provided with a tubulure for exhaustion at E (the tube being nearly one meter in length), could be inserted in either beam. The arc light or sunlight enters at the slit S of the collimator C . The direct beam for adjusting the interfer-

ences is observed with the telescope at L' and the interfering diffraction spectra by the same telescope on being rotated into the position D . The sodium line from the two coincident spectra is an admirable fiducial mark to which the centers of ellipses, as they move across the field, are always referred. A fine horizontal wire across the slit enables the observer to place the spectra in coincidence both horizontally and vertically.

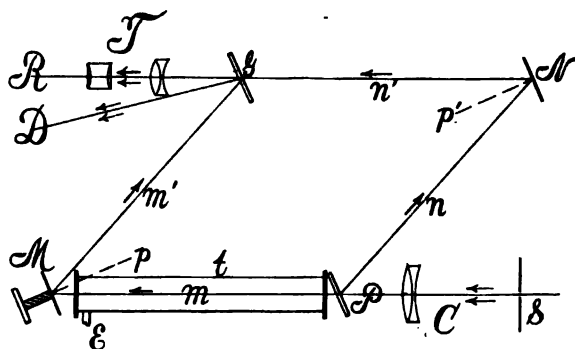


FIG. 1.

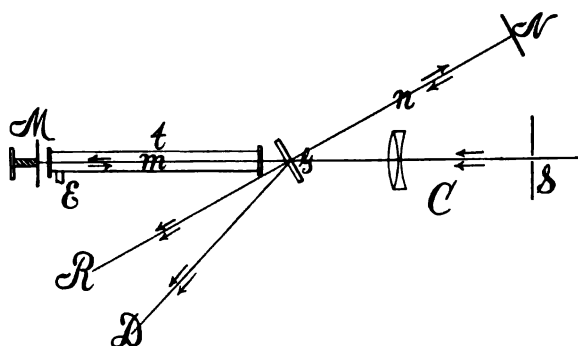


FIG. 2.

As in the earlier instrument,* the arms m and n were made of gas pipe, through which a current of water continually circulates, when necessary. Tremors of course could not be wholly eliminated; but the instrument, in spite of its lightness, was made firm by the aid of horizontal and vertical leveling screws, which imparted slight strains to the gas pipe arms m and n ; *i. e.*, the ends at M and N were pushed away from the wall by horizontal screws until sufficient strain of parts resulted, while at the same time they were lifted above the table carry-

* This Journal, xxxiii, 1912, pp. 107-108.

ing the tripod (below G), by similar screws acting vertically. The latter, moreover, were advantageous in bringing (raising or lowering) the center of ellipses into the center of the field, after an approximate adjustment had been made. Similarly the foot of the revolving arm, which supports the telescope at D , could be used for the same purpose with advantage.

An open collimator at C , *i. e.*, objective and slit each in opaque screens, is specially convenient, inasmuch as it allows the image of the slit S reflected at M to be visibly reproduced on the jaws of the slit. The occurrence of parallel light and of a beam of light normal to M are thus both put in evidence. If m is cut off, the same applies to the mirror N and beam n , though this is liable to be too dark and the rough and fine adjustments are best made at the telescope, using a wide slit first. The collimator C should be long, in other words, the lens of long focal distance, so that the beam m passing through the tube may remain very short or spot-like in its vertical dimensions. Otherwise too much is cut off by the tube and reflection from G before the beam enters the telescope.

With the arc lamp the spectrum may be darkened, so that the sodium lines stand out clearly, by raising or lowering the arc behind the black screen, with a hole about one centimeter in diameter for the passage of light. A small swiveled screen in front of the objective telescope, and approached from one side, greatly sharpens the interferences and the Fraunhofer lines by cutting off undesirable light and particularly the stationary interferences. Possibly the latter would disappear if the plate of the grating were made very thick. When water circulation is used, some time must elapse before the temperature conditions are adequately stationary. With distances m and n as long as the above, the ellipses are rarely perfect, and frequently appear coarse and distorted. It is nevertheless easy to adjust the center of ellipses with an error not larger than $\cdot 000,05$ centimeter, at the micrometer screw M , *i. e.*, to about the mean wave length of light.

3. *The Same. Results.*—The sealed glass tube, t , of length $e = 89.49$ centimeters within, having been inserted, the data for the refraction of air found by alternately exhausting and filling it were about as given in Table I.

TABLE I.

Glass tube with plate-glass ends; diameter, 4.5^{cm} ; length, 89.49^{cm} .
Barometer, 75.59 at 17.5° ; temperature, about 20° .

p_0	p	$10^5 \Delta N$	$\mu - 1$
75.59	.32	2505	280
----	.10	2495	279

Here ΔN is the displacement of the micrometer corresponding to the pressure difference $p_0 - p$, at the constant temperature given, and μ the index of refraction of the air contained.

The induction coil was now attached and a current from 3 to 4 storage cells sent through the apparatus. Not the slightest shifting of ellipses or interference lines could be detected when the secondary current was alternately made and broken. The lines were very clear. The experiment was then repeated and the air pump (Geryk) connected directly with the tube without accessory apparatus between. A coarsely stratified column and some cathode dark space was obtained. But the effect at the interferometer was again definitely negative.

The absence of an effect due to the current was to be expected, since the positive and negative currents and the direct beam of light both traveled in opposite directions. The same is true for the ionization, which is too slight; but it was supposed that some evidence of a temperature effect might be obtained; but there was none.

$$\text{Since } p = C(\mu - 1)\theta = C\Delta N\theta/e,$$

where C is constant and θ denotes absolute temperature, therefore at constant pressure

$$\frac{d(\Delta N)}{\Delta N} = \frac{d\theta}{\theta}$$

$$\text{if } d(\Delta N) = 5 \times 10^{-3} \text{ cm., } \Delta N = 25 \times 10^{-3} \text{ cm.,} \\ \theta = 293^\circ, d\theta = .59^\circ;$$

so that whatever rise of temperature may have occurred must have been much less than .6° Centigrade.

4. *Second Experiments. Apparatus.*—In this experiment the direct and return beams m and n were separated as shown in fig. 2, into m and m' and n and n' , the beams traveling along contiguous sides of a rhombus. M and N are again the two opaque mirrors, the former with micrometer; C is the collimator, open as in fig. 1. The grating above the tripod of the interferometer has been removed and replaced by a plate of glass P of about the same thickness, while the grating is at G diametrically opposite, with its ruled face toward N . The normals of the mirrors are shown at p and p' , and the telescope is either at R (direct ray) or at D (diffracted ray). It is here convenient to have two telescopes, one set at R and the other at D .

To secure this adjustment the interferometer of fig. 1 is provided with a cross arm of gas pipe under $P'G$, which can be clamped firmly in place on the standard of the tripod, below P in fig. 2, or G in fig. 1. The end of the arm below G , fig. 2, has a foot with a vertical set screw for imparting strain, and is

braced with slight strain against rotation around the cross arm. In the same way M must be laterally braced with slight strain against rotation around the arm under N or NP .

The arm of the telescope R , in fig. 1, is in this case turned about P , the telescope being simultaneously rotated until it occupies the position D in fig. 2. It is for this reason that two telescopes are used, as it would be much less convenient to provide a special axle moving about the foot of G .

To adjust the apparatus the arms m' and n' are first made roughly equal with a scale. P and G are then placed in the same line by a straight edge, the slit is widened so that the beam m passes directly through central parts of P and the reflection (spot) from the central part of the mirror M is seen to strike the central part of the grating G . Proceeding thence, the beam is reflected into the telescope T , approximately in position (both M and G being rotated horizontally and vertically for this purpose, finally by the adjusting screws). Next the beam reflected from P is made to strike the central parts of the mirror N (which it should do at once on very slight rotation of P), from which it is reflected to the central parts of the grating G , so that the two beams m' and n' may be across the same vertical line. Finally, G is adjusted until the two direct images coincide accurately (both horizontally and vertically) in the telescope, a fine hair having been drawn across the slit, as above.

Under these circumstances there will be four direct images in the telescope at R , due to front and rear reflection at P and G , neither of which is optical plate; but there will be but three spectra or three sodium lines visible at D , since the ray reflecting the rear face of G is not diffracted. To obtain the interferences, a single spectrum line from M must be placed fully in coincidence with either of the two lines from N ; but to find them is nevertheless a matter of considerable difficulty. Since reflection takes place not from one and the same face of glass, but from the two independent faces P and G , the ellipses in the field of view are liable to be very eccentric. They thus appear as the merest hair lines, easily overlooked even when M has (by trial) been moved into the correct position. In fact, if the sodium lines be called

$$Na_m, \quad Na_n, \quad Na_n,$$

I have only been able to get interferences from two of these, say Na_m, Na_n , but not from Na_m, Na_n , after wasting much patience in the attempt. There may be some other reason for this which has escaped me. Na_m passes through three thicknesses of glass, whereas Na_n and Na_n pass through one and three thicknesses, respectively, and I have not been able to

ascertain whether the self-compensating case or the other is the one which succeeds. In fact the four lines $m\ m'\ n'\ n$ are not necessarily coplanar, but will lie on a ruled surface, which is to be made as nearly plane as possible. Thus the plates P and G may be clamped to a long strip of plate glass, or other devices employed. These succeed adequately after some readjustment, but I have not been able to place the center quite in the center of the field of view. Experimentally this is not necessary; for the eye is quite as sensitive in placing the horizontal element of the circle in coincidence with the fiducial sodium lines (which it intersects at right angles), the inclination on the two sides being in opposite directions. Naturally the interference bands should be strong.

The micrometer screw of M , in this case, bisects the acute angle of the rhombus of $\phi=30^\circ$, and the motion of the mirror over ΔN here cuts off $2\Delta N/\cos 15^\circ$ from the beam of light. Moreover, at the grating the beam of light is shifted laterally when M advances, by an amount $\Delta N \tan 15^\circ$ so that $2\Delta N \sec 15^\circ \sin^2 15^\circ$ is restored. Thus the path difference produced is generally $2\Delta y = 2\Delta N \cos \phi/2$.

5. *The Same. Results.*—The data obtained in case of the rhombus are given in Table II.

TABLE II.

Glass tube as in Table I. Barometer, 76.0 centimeters.

p_0	p	$10^5 \Delta N$	$10^5 \Delta y$	$\mu - 1$
76.0	.4	1285	1241	287
---	---	1280	—	286

The data are of the same order as the preceding table, remembering that the tube is not twice traversed by the beam of light, as is the case with the adjustment of Table I.

The current from the induction coil was now passed through the exhausted tube and the circuit made and broken. Not the slightest effect could be observed, the interferences remaining stationary in all parts of the field, just as in the preceding case.

The endeavor must now be made to exhaust the tube to the highest degree possible, and to pass the current between electrodes of very high potential difference. To this I hope to return at some other opportunity.

Brown University, Providence, R. I.

ART. X.—*Electrolytic-Analysis with Platinum Electrodes of Light Weight*; by F. A. GOOCH and W. L. BURDICK.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—cexxxii.]

THE present cost of platinum, which is the ideal substance for anodes and cathodes in most processes of electrolytic analysis, is now so considerable that many attempts have been made to substitute for that metal other less expensive materials. Medway* has shown that a crucible of silver may replace the platinum crucible used as a rotating cathode in determinations of copper; Sherman† has proposed the use of tin vessels for cathodes in several processes; Turrentine‡ has shown that dishes of graphite saturated with paraffine may be of service for approximative purposes; and other devices have been suggested. No material has, however, been found so suitable for general electrolytic work as platinum. Our attention has been directed, therefore, to the devising of forms of apparatus which, while suited to the purposes of exact electrolytic analysis, require the least amount of this expensive metal. We have experimented, first, with thin films of platinum deposited upon glass, and, secondly, with diminutive electrodes of platinum gauze or foil of ordinary thickness and stability. All of these electrodes were designed for use as rotating cathodes, with a view to securing the best and most rapid deposition.

Electrodes of Platinized Glass.

The ordinary method of making gas-electrodes (which consists in painting glass with the usual platinizing solution, drying the coating for a long time in the current of warm air above a low flame, and finally heating strongly, even to redness) does not produce films of platinum sufficiently adherent for service as the cathode in the electro-deposition of metals. Such films flake off in the electrolytic process and are removed from the glass when the deposited metal is subsequently dissolved by a suitable reagent. It was found, however, that a much more closely adherent film may be obtained when a viscous mixture of glycerine and dry chloroplatinic acid is substituted for the usual plating solution. The mixture is applied by means of an asbestos swab to the glass previously raised to a temperature sufficient to volatilize the glycerine immediately, and the resulting film of metal is burned into the glass at the softening point of the latter. Various forms of electrode suitable for use as rotating

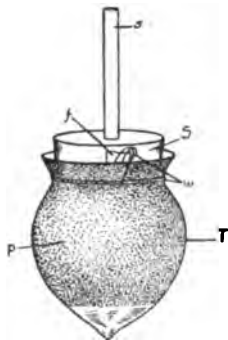
* This Journal (4), xviii, 180.

† Jour. Am. Chem. Soc., xxix, 1065.

‡ Trans. Am. Electrochem. Soc., xv, 505, 1909; xvii, 303, 1910.

cathodes were made in this manner, and tested. A straight tube with open end, an ordinary test-tube, the bulb'd tube, and the cup made from a thistle tube are all serviceable: but the last, shown in figure 1, is most convenient in use. This electrode is easily made by platinizing the thistle *T* of a lead glass thistle-tube about 3.5^{cm} in diameter, and then drawing out and sealing off the straight tube at its junction with the thistle. The electrode is fitted to a perforated rubber stopper *s*, which is slipped tightly over the vertical shaft of the motor. The shaft carries the current, and the electrical connection is made

FIG. 1.



between the shaft and the platinum film *p* by means of foil *f* attached to the former and wire *w* twisted about the latter, the wire and foil being pressed into contact between the glass and the stopper. Before using, the electrode is rinsed thoroughly in hot nitric acid, washed with water, dried in an air bath, and weighed.

Following are the results of tests in which these electrodes were used as the cathode rotating at the rate of about 300 revolutions to the minute. The anode was platinum foil placed vertically, and the electrolyte, 50^{cm}³ in volume, was contained in a beaker. The solution of electrolyte was in each case standardized by electrolysis with the rotating platinum crucible used as cathode.

*Electrolysis of Copper Sulphate.**

Copper taken gram.	Copper found gram.	Error gram.	Initial current		Approx. N.D. ₁₀₀	Time min.
			amp.	volt.		
Platinized test-tube used as cathode.						
0.1279	0.1277	-0.0002	2	..	10	30
0.1280	0.1278	-0.0002	1.8	..	9	30
0.1272	0.1272	0.0000	2	..	10	30
Platinized tube, open at end, used as cathode.						
0.1272	0.1265	-0.0007	2.1	5.5	10.5	40
0.1272	0.1265	-0.0007	2	5.5	10	40
0.1272	0.1772	-0.0000	1	6	5	30
Platinized thistle-tube used as cathode.						
0.1272	0.1272	-0.0000	2	5.5	10	30
0.1272	0.1265	-0.0007	30
0.1272	0.1266	-0.0006	30
0.1272	0.1268	0.0004	30

* Acidulated with H₂SO₄.

*Electrolysis of Nickel Ammonium Sulphate.**

Nickel taken gram.	Nickel found gram.	Error gram.	Initial current		Approx. N. D. ₁₀₀	Time min.
			amp.	volt.		
Platinized test-tube, used as cathode.						
0.0746	0.0744	-0.0002	0.8	7.5	4	40
0.0746	0.0743	-0.0003	1.2	--	6	35
0.0744	0.0744	0.0000	1.2	--	6	50
0.0743	0.0739	-0.0004	1	7.5	5	30
0.0743	0.0742	-0.0001	0.6	7.5	3	40
Platinized thistle-tube, used as cathode.						
0.0742	0.0741	-0.0001	1	5	5	30

* With addition of 1 gram. of $(\text{NH}_4)_2\text{SO}_4$ and 25^{cm} of concentrated ammonia.

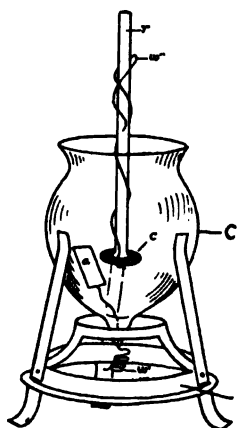
These results show that the inexpensive apparatus described is capable of yielding good results. The chief difficulty lies in the tendency of the film to disintegrate when the deposited metal is subsequently dissolved off the electrode, so that after a few successive determinations the film needs to be renewed. There is, moreover, some tendency to the disengagement of particles during the process of electrolysis, and this no doubt accounts in great measure for the negative errors noted above. It was shown in other experiments that this loss of cathode material is likely to be greater, possibly amounting to as much as 2 to 3^{mm}, when the films are too much reinforced by the application of several successive layers of the plating mixture. The weight of platinum in the films used in the experiments described above did not exceed 0.2 gram. spread upon a surface of approximately 20^{cm}². The entire weight of platinum in the film and connecting wire of the cathode amounted to about 0.7 gram. It is probable that the slight losses due to the cathode disintegration in the course of an analysis might be reduced by the use of the filtering device to be presently described; but the use of small electrodes and a weighable cell proved to be so much more convenient that the experiments with the platinized glass were carried no further.

Electrolysis with Small Electrodes in a Weighable Cell.

If the current directly employed in electrolytic analysis is high, as is inevitable in rapid processes in which small electrode surfaces are employed, the deposits of metal lack compactness and are likely to be disengaged from the electrode. The apparatus to be described was devised to retain and gather the detached material so that it may be weighed with the remainder of the cathode deposit. The device, shown in figure 2,

consists of a 35^{cm} cell *C* made from a thistle-tube. The anode *a* is a small piece of thin platinum foil, about one centimeter square, welded to a platinum wire *w'* which is sealed into the thistle, as shown. The cathode *c* consists of a disc of gauze or foil, also about one centimeter square, carried by a rod *r* of lead glass which is fused into the meshes of the gauze or into a central hole in the foil, an arrangement which gives great rigidity without the use of much platinum. The electrical connection between the disc cathode and the shaft, which

FIG. 2.



carries the current, is made by a platinum wire *w''*. A stand *s* of spring brass holds the cell during the process of electrolysis, and a similar lighter stand (best made of sheet aluminium) serves to support the cell and contents upon the balance pan. In order to show details clearly, the cell is represented in the figure as resting lightly upon this frame. In actual use, the cell is pushed downward as far as possible, and is held rigidly.

In using this apparatus, the cathode cell is washed, dried, and weighed. The material for analysis, dissolved in about 15^{cm} of liquid, is placed in the cell. To prevent possible loss of liquid by spattering, a collar (conical) cut from a funnel or (concave) made from a perforated and split watch-glass, is set upon the rim of the thistle. The glass rod of the cathode is fixed to the motor shaft. The electrical connections are made as shown. The cathode is rotated at about 300 revolutions per minute.

Electrolysis of Copper Sulphate with rotating cathode ;
cell and disc cathode washed by decantation.*

Copper taken grm.	Copper taken grm.	Error grm.	Initial current		Approx. N.D. ₁₀₀	Time min.
			amp.	volt.		
0.1272	0.1269	-0.0003	2	5.5	100	20
0.1272	0.1278	+0.0006	1.5	7	75	20
0.1272	0.1280	+0.0008	2	4.5	100	20
0.1272	0.1270	-0.0002	2	7	100	20
0.1272	0.1271	-0.0001	1.2	5	60	20

Acidulated with H₂SO₄.

At the end of the electrolysis the cathode is disconnected from the shaft and washed in the cell. Loose particles of the deposit are allowed to settle, and the supernatant liquid is decanted. After washing by decantation with water, and finally with alcohol, the cell and cathode are dried in the air bath, and weighed. Data and results of the procedure applied to copper sulphate, standardized by means of the rotating crucible, are given on the preceding page.

The results are reasonably good, but the difficulty of washing thoroughly by decantation without loss of any loose particles, and with complete removal of the washing liquid so that the drying process need not be prolonged unduly, is considerable. To meet this difficulty we make use of the little filter tube shown in figure 3. This is made by fusing the end of a lead glass tube, flared slightly, to a little disc of platinum foil perforated by a sharp point, the rough edges of the perforations being turned outward. By applying the suction of the filter pump to the open end of the tube, and dipping the disc end into an emulsion of asbestos, a felt of asbestos is deposited upon the perforated disc. The tube and felt may be dried, and even ignited, without difficulty.

This little reverse filter is dried and weighed with the cell and cathode ready for use. The electrolysis is made in the manner previously described. The liquid of the cell and the washings of the cathode and cell are drawn off through the reverse filter. The stand, cell, cathode, and reverse filter, shown in figure 4, are dried and weighed together. Results of this procedure, applied to the determination of copper in copper sulphate and of nickel in nickel ammonium sulphate, are given in the table below.

For comparison, a few determinations were carried out, otherwise similarly, without rotation of the cathode. In this case the deposit was much more bulky, rather difficult to dry thoroughly, and perhaps more sensitive to oxidation. Results obtained in this manner are also given in tabular form.

FIG. 3.

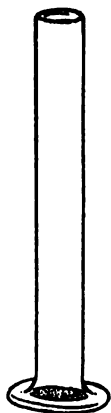
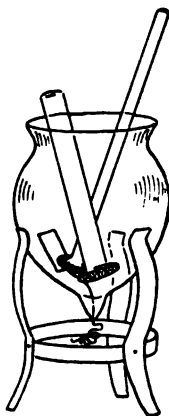


FIG. 4.



Electrolysis with Rotating Cathode: cell, disc, cathode, and reverse filter, weighed together.

Determination of Copper.

Metal taken grm.	Metal taken grm.	Error grm.	Initial current		Approx. N.D. ₁₀₀	Time min.
			amp.	volt.		
0.1272	0.1273	0.0001	1	5	50	20
0.1272	0.1276	0.0004	1	5	50	20
0.1272	0.1272	0.0004	1.2	5	60	20
0.1272	0.1274	0.0000	1.2	5	60	20

Determination of Nickel.

Metal taken grm.	Metal taken grm.	Error grm.	Initial current		Approx. N.D. ₁₀₀	Time min.
			amp.	volt.		
0.0743	0.0743	0.0000	0.6	6	30	30
0.0743	0.0744	+0.0001	0.8	8	40	30
0.0748	0.0744	-0.0004	1	10	50	30
0.0743	0.0738	-0.0005	1	7	50	30
0.0748	0.0741	-0.0002	1	7	50	30

Electrolysis of Copper Sulphate without rotation of the cathode: cell, disc, and filter weighed together.

Copper taken grm.	Copper taken grm.	Error grm.	Initial current		Approx. N.D. ₁₀₀	Time min.
			amp.	volt.		
0.1272	0.1282	+0.0010	1.2	6	60	35
0.1272	0.1282	+0.0010	1.1	5	60	30
0.1272	0.1276	+0.0004	2	5	100	30
0.1272	0.1275	+0.0003	2	5	100	30

It is obvious that the process without rotation is inferior in point of accuracy to the otherwise similar process in which the cathode is rotated.

The construction of the apparatus is very simple and the use very easy. The weight of stand, cell, cathode, and filter tube together need not exceed 17 gms. to 18 gms.; and that of the platinum used need not be more than 1 grm.

The results are best and most rapidly obtained when the cathode is rotated, but this device may be relied upon to yield reasonably accurate determinations when a rotating motor is not available.

ART. XI.—*The Siliceous Oölites of Central Pennsylvania*;
by VICTOR ZIEGLER.

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Summary of Literature.—The occurrence of siliceous oölite in Center County, Pennsylvania, was first noted by Rogers in the report of the First Geological Survey of Pennsylvania. In a brief statement, Rogers calls attention to the extreme scarcity of oölitic chert and its occurrence here. D'Inwilliers in the report on Center County, of the Second Geological Survey of Pennsylvania, also merely calls attention to this occurrence, and notes the presence of oölitic limestone in this region. Barbour and Torrey, in 1890,† first gave a description of the structure of the siliceous oölite as revealed by the microscope, and analyses of the same. To E. O. Hovey, however, belongs the credit of making the first thorough study of these rocks and of first applying the petrographic microscope to their interpretation. Hovey‡ arrives at the conclusion that the oölites are the result of deposition from the silica-laden waters of hot springs about a nucleus of sand. Wieland,§ in 1907, discussed briefly this and related oölitic rocks and arrived at the same conclusion as Hovey in regard to their origin. As especially important he regards the occurrence of chert boulders of peculiar concentric structure in the area of less than one square mile within which the oölites are found. These he considers “the rims of hot springs and geysers on the low-lying shore of the Calciferous.” Wieland states that “the dissolved silica first deposited would have formed rings; that deposited while in more rapid motion the small spheruled oölite, which is most plentiful near the best marked of the rim boulders. Lastly would be formed large-grained oölite, the compact and pure quartzite, which is the handsomest oölite known.” E. S. Moore, in a paper read before the British Association for the Advancement of Science in 1911, regards the

* The thanks of the author are due to Professors James F. Kemp and C. P. Berkey for kind and valuable suggestions.

† This Journal (3), vol. xl, p. 246.

‡ Bulletin of the Geological Society of America, vol. v, p. 627.

§ This Journal (4), vol. iv, p. 262.

siliceous oölite as being a replacement of the oölitic limestones occurring within this area.*

All of the above papers, with the exception of the last, were based on loose material occurring within a very limited area north of State College (see fig. 1). In fact, it was long sup-

FIG. 1.

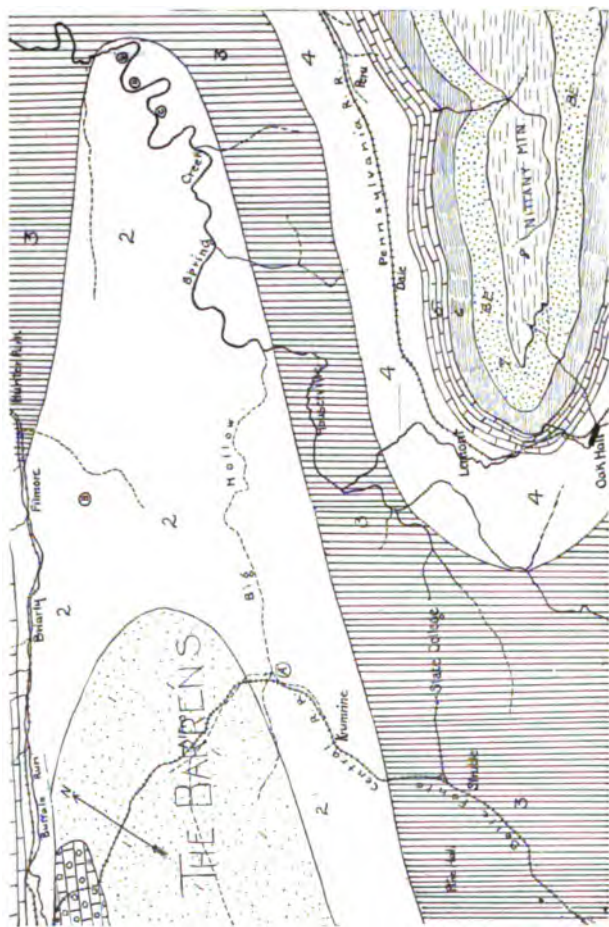


FIG. 1. Map of part of Center County, Penna. Scale, 1 inch = 2 miles.

- 1 = Upper Cambrian S. S., showing at base the U. C. limestone.
- 2 = Beekmantown limestone.
- 3 + 4 = Chazy limestone.
- 5 = Black River and Trenton limestone.
- 6 = Utica and Lorraine.
- 7 = Bald Eagle conglomerate and sandstone.
- 8 = Juniata red shale + sandstone.
- A, B, C, D, E = Exposures of siliceous oölite beds.

posed that no exposure of the oölite existed, but that the loose pieces were the result of the erosion of the overlying strata. In the fall of 1910, G. E. Anderson located the first exposure in a railroad cut north of State College. Subsequently, while

* *Journal of Geology*, vol. xx, p. 259, 1912.

engaged in field work during the spring and summer of 1911, Mr. Anderson and the author found a number of outcropping beds of siliceous oölite in place. Hence, now for the first time, the exact relation of the siliceous oölite to the rocks of the area can be determined accurately. Similar siliceous oölites occur near Tyrone on the Little Juniata River, and have also been noted by Stosef in the Mercersburg—Chambersburg quadrangle in the southern part of the state. The geologic conditions both at Tyrone and at Chambersburg are essentially the same as in Center County.

Occurrence and Distribution.—Both calcareous and siliceous oölite occur in Center County. The calcareous oölites, as a rule, are massive oölitic limestones of dark gray to blue color, with small, well-rounded spherules. Occasionally they are also dark gray, slightly crystalline, and have small dark green oölites. The siliceous oölite occurs interbedded in thin irregular layers in the limestone, and also in irregular chert concretions and nodules in some rare limestone layers. As far as observed, the oölite beds are confined to the Ordovician and Cambrian strata, which may be subdivided as follows in Center County :

7. *Utica and Lorraine Shale*, 1200 feet.

Gray, sandy shale, and intercalated, gray, resistant sandstone layers in upper part. Unfossiliferous.

Black, fissile, and calcareous shale below, fossiliferous.

6. *Trenton Limestone*, 600 feet.

Dark black, and blue, blocky limestones with interbedded shale layers and crystalline gray limestones, usually fossiliferous.

5. *Black River Limestones*, 100 feet.

Compact, very pure, dove-colored limestone, with few fossils at top, below almost black even-fracturing limestones, fossiliferous. Shaly layers at bottom.

4. *Chazyan*, 2300 feet.

Compact, dense, light gray, dolomitic limestone with chert nodules at top, unfossiliferous in part. 1200 feet shaly limestones, interbedded with massive, pure, and crystalline, blue limestones at base. Occasional oölitic limestone beds. Fossiliferous.

3. *Beekmantown*, 2400 feet.

Series of highly shaly, laminated limestones, with many shale partings. The limestones, as a rule, are clastic "Edge-wise" and other conglomerates. Shale partings are often ripple-marked and show suncracks. Fossils rare in upper portion. At base interbedded sandstone lenses. Some oölitic limestone in lower portion, and siliceous oölite layers throughout.

* U. S. Geol. Survey, Folio No. 170.

2. *Upper Cambrian Sandstone, 500–600 feet.*

Pure, white sandstone, poorly cemented and friable, rarely quartzitic. Shows distinct, thin, and even bedding. The grains are pure, well-rounded sand. In lower portion, gray, and occasional red to brown, tough quartzite, highly and irregularly cross-bedded.

1. *Upper Cambrian Limestones (base not exposed).*

Oölitic limestones; dark gray to blue, sandy, and shaly limestones. Bedding planes, distorted, and irregular. Layers of *Cryptozoon proliferum* abundant, also trilobites and brachiopods (*Dikellocephalus newtoni* and *Lingulepis* sp.?).

The exact number of horizons of siliceous oölite it is difficult to state. In one section of the Beekmantown limestones eleven definite layers were exposed. This section represents only about 139 feet near the top of the formation. Outcrops of the calcareous oölites are not at all rare, but good exposures of the siliceous occur only in a few localities (see fig. 1). As a rule the siliceous oölite occurs in loose fragments in mantle rock, especially in the area indicated, while most of the Beekmantown limestones have been removed by erosion, and only the resistant layers of oölite remain. The sandy area underlain directly by the Upper Cambrian sandstone furnished all the oölite specimens from this locality, which in all cases were fragments of loose boulders.

The Structure of the Oölite-bearing Rocks.—As will be evident from the accompanying map, the rocks are folded into an anticline pitch-down toward the northeast. The oldest rocks on the area are hence shown in the extreme northwest corner of the map where Upper Cambrian limestones have been brought up by a thrust fault. From this core northwestward we get the parallel fringes of the younger formations. Nittany Mountain in the southeast corner of the map is the result of a synclinal pitch towards the east.

Typical Detailed Section of Oölite Horizon.—The finest section of siliceous oölite occur in the gorge of Spring Creek, four or five miles south of Belle Fonte. The following is a detailed section of the best exposure:

- 31. 50 feet. Gray, thin, and irregularly bedded limestone, with edgewise limestone conglomerate, carrying in upper portion Rastrites, near *R. barrandi*. In the basal portion we have a thin layer of siliceous oölite, underlain by dense sandy limestone.
- 30. 2 feet. Dark gray, slightly oölitic limestone.
- 29. 2 feet. Light gray, very dense limestone.
- 28. 7 feet. Dense, blue limestone, with conchoidal fracture, carrying black chert concretions.
- 27. 4 feet. Impure, dark gray limestone.

- 26 .3 feet. Dense gray limestone, carrying five distinct bands of siliceous oölite. The oölitcs are small.
25. 8 feet. Dense, gray, shaly, and laminated limestone.
24. 2 feet. Oölitic limestone of mottled appearance.
23. 6 in. Layer of siliceous oölite.
22. 5½ ft. Dense, black, shaly limestone, interbedded with gray, crystalline, dolomitic limestone.
21. 10 in. Dark blue, dense l.s. in upper part with white, oölitic chert concretions.
20. 15 in. Dense, black crystalline l.s. with chert concretions, oölitic in thin sections.
19. 10 in. Dark blue, dense l.s. with gray chert concretions.
18. 8 in. Siliceous oölite, made up of white quartz spherules with a calcareous cement, acting as a matrix of pebbles, of dense gray l.s. and of pure white sandstone at base.
17. 8 feet. Alternating, very dense, dark, and light gray, laminated limestone, with occasional chert nodules.
16. 3 in. Black, oölitic chert.
15. 18 in. Black, coarsely crystalline, l.s., with vugs, and small calcite seams.
14. 2 feet. Dense, gray, dolomitic limestone, with conchoidal fracture.
13. 2½ ft. Mottled shaly limestone.
12. 3½ ft. Dense, finely banded, light gray, dolomitic limestone.
11. 3 feet. Dark blue, oölitic, finely laminated limestone, containing in its lower portion pebbles of the underlying light gray limestone. The line on contact is irregular.
10. 5 feet. Light gray, dolomitic limestone with conchoidal fracture.
9. 4 feet. As above, but blocky, and smooth breaking.
8. 2 feet. Dense, black limestone.
7. 6 feet. Dark gray, crystalline limestone with chert concretions. At top a breccia of limestone fragments cemented by well-crystallized calcite, probably a collapsed cave.
6. 3 in. White-grained, black, siliceous oölite carrying enclosed dense, black chert concretions which are oölitic under crossed nicols.
5. 16 in. Dense, gray limestone.
4. 10 in. Light gray, siliceous oölite, carrying also fragments of an older, darker oölite-horizon as pebbles.
3. 6 feet. Dense, gray, slightly crystalline limestone and dolomite.
2. 7½ ft. Covered.
1. 4 feet. Light gray limestone with irregular and angular pieces of oölitic chert.

Total, 139 ft. 3 in.

All of the oölite layers in this horizon are fairly definite, and are exposed for about ten or fifteen feet along the bedding planes. Over this distance they maintain a fairly uniform character and thickness. Layers Nos. 1, 4, and 6 show contemporaneous erosion of some oölite horizon, and its redeposition in a limestone matrix in layer No. 1, and in an oölite

FIG. 2.

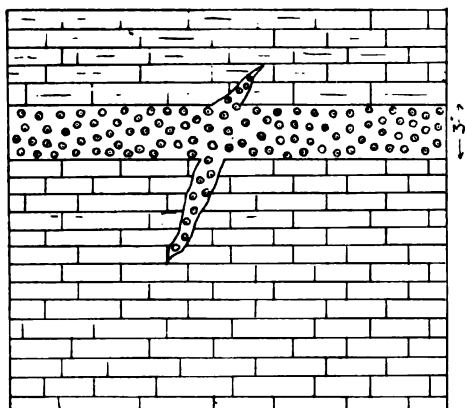


FIG. 3.

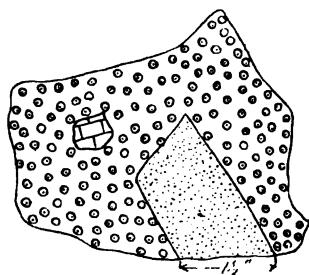


FIG. 2. Siliceous oölite layer on Spring Creek.

FIG. 3. Fragment of siliceous oölite, coarse, showing included fragment of limestone and of fine-grained siliceous oölite.

horizon in the other two. No. 11 also shows contemporaneous erosion, in this case, of one of the limestone layers. Fig. 2 shows the occurrence of oölite in No. 31, and fig. 3 a specimen from layer No. 4, and shows the association of the two different oölites.

Petrographic description of the Oölites.—Several distinct types of siliceous oölite exist in this area, and they will be described in order. As may be noticed from the accompanying map, the name of the locality is applied to the occurrence.

Type One: the Filmore phase.—The specimens were collected about one-and-one-half miles south of Filmore, and occur here as loose fragments, and in one doubtful exposure.

The oölites are here fairly variable in size and in shape, and as a rule are mixed with many flat and lense-like grains, which appear essentially like lentils, are somewhat imperfectly cemented, and consist of quartz. The nucleus is in nearly all cases a grain of quartz, usually of irregularly, rounded, and elongated shape. Sphericity of grains is notably absent, and

many grains are angular. At times the nucleus is made up of several grains of quartz. The quartz enlargement of the sand-grain nuclei is fibrous chalcedony, and also the fine chert mosaic deposited in concentric rings, as many as twelve being faintly visible. A few of the quartzes show resorption, presumably by solution which subsequently served to enlarge them, partly replacing the original grain with chalcedony. The same process is indicated by the absence of definite outlines in some sand grains and their tendency to pass by insensible gradations into the fibrous chalcedony. Many of the oölites are entirely chert or chalcedony, and have completely replaced the nucleus; but even in this case, under crossed nicols the outline of the quartz grain which served as a center of deposition is faintly visible. The quartz-grains appear to be igneous in origin and carry fine trails of dust, and very small inclusions of a mineral

FIG. 4.

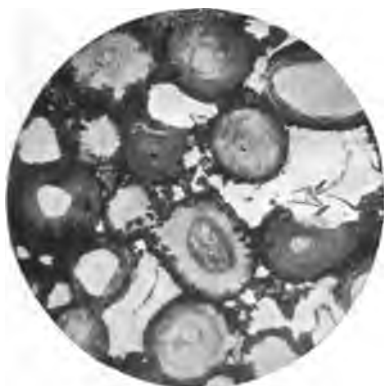
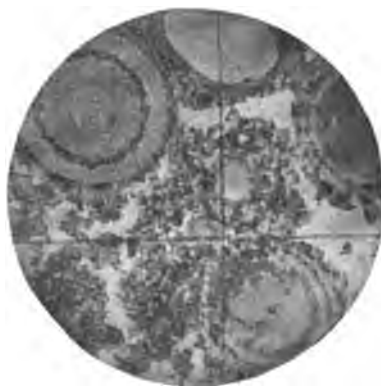


FIG. 5.

FIG. 4. Filmore type of siliceous oölite. $\times 72$.FIG. 5. Krumrine type, at contact between calcareous and siliceous oölite. $\times 32$.

apparently biotite. Fibrous chalcedony also fills most of the interstices between the oölites, and is usually in indistinct bands parallel to their general outline. Some of the quartzes show a tendency toward secondary enlargement. Very little calcite is present, and that seems to be a secondary infiltration subsequent to the oölite formation. The sand nuclei vary in size from minute fragments up to $.62\text{mm}$ in diameter. The longer diameter often exceeds the shorter four or five times.

Type Two: the Altro phase.—The siliceous oölite occurring in the vicinity of Altro is the handsomest in Center County. It is practically pure quartzite in composition, as shown by the following analysis by Wieland:*

* This Journal (4), iv, p. 262.

SiO ₂	99·10%
Fe ₂ O ₃	·11
Al ₂ O ₃	·17
CaO	·39
H ₂ O	·25
	<hr/>
	100·02%

The color is a beautiful light gray, and the grains are well rounded, as a rule spherical; under the microscope they show usually a quartz nucleus surrounded by layers of a very fine mosaic of chert. The individual spherules are nearly uniform in size and are cemented by fibrous chalcedony often laid down in parallel layers. The layers making up the oölite and the cement are alternating black and white. The relative proportion of black and white layers present give the color to the

FIG. 6.

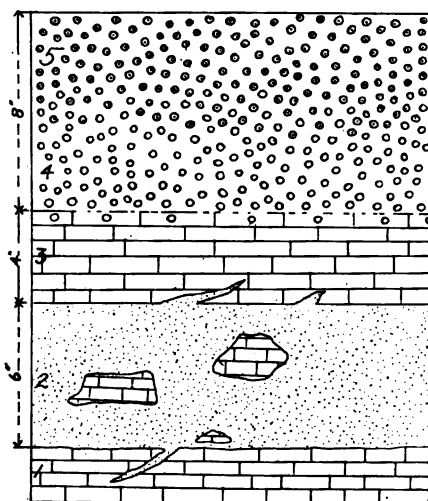


FIG. 6. Section of oölite near Krumrine. 1 and 3, dense, siliceous limestone; 2, pure white quartz sandstone; 4, calcareous oölite; 5, siliceous oölite.

oölite; dark oölite with white grains being due to the greater abundance or thickness of the black layers; white oölites with predominant black grains, in turn, resulting from the excess of light-colored layers in the oölite and the cement.

Type Three.—Occurring about one mile north of Krumrine. In a cut along the track of the Belle Fonte Central R.R., a small exposure of oölite gives the following section illustrated by figure 6.

Figure No. 5 shows a thin-section taken at the contact line between the calcareous and siliceous oölite. A study of the thin-section reveals the fact that the oölites, which are calcareous, in all cases show a distinct nucleus of one or more small rounded quartz grains, while the siliceous oölites only rarely have the nucleus preserved, but usually show its replacement by fibrous chalcedony or a very fine aggregate of chert. This would seem to indicate that silica-laden waters are here replacing a calcareous oölite.

An analysis of an oölite specimen of this type gave E. H. Barbour the following result : *

	Calcareous Oölite.	Siliceous Oölite.
SiO ₂	3.70 %	56.50 %
Al ₂ O ₃ }	1.42	1.50
Fe ₂ O ₃ }		
CaCO ₃	88.71	16.84
MgCO ₃	8.09	2.60
H ₂ O		12.54
Spec. gravity	2.654	2.688

Type Four.—In addition to the above types of occurrence we have one at least 1200' above the highest definite siliceous horizon found in place. Several excellent sections of the intermediate strata are available, but no oölitic chert was observed. In this horizon the oölites occurred in chert concretions, while in the others definite layers are the rule (fig. 15). They are fresh, occurring in a very recent road-cut along Spring Creek about two miles south of Belle Fonte. They are made up of two separate layers, an outer dense cherty and an inner calcareous one, and in several also show a chert nucleus. The inner ring is composed of a coarse crystalline material showing separate faces up to one-half inch in diameter, which are penetrated by a fine dotted-like intergrowth strongly suggesting graphic structure. Under the microscope the outer ring, the nucleus, and the dotted intergrowth prove to be quartz, while the crystalline matrix of the latter is coarsely granular calcite showing well-defined twinning striations.

The limestone is oölitic (fig. 11). Distinct nuclei could be discerned, but it was impossible to determine their exact character, except that they were predominately calcite with traces of silica apparently crushed together. There is no uniformity in their shape; circular, elliptical, both straight and curved rod like, and more irregular types were present. The oölitic structure is probably syngenetic with the formation of the

* This Journal (3), vol. xi, page 246.

FIG. 7.

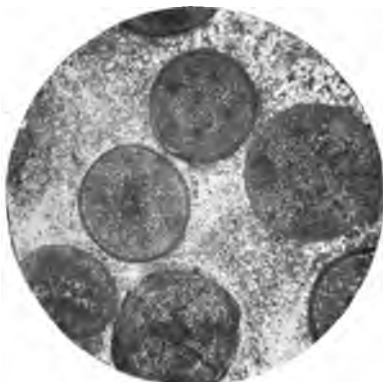


FIG. 8.



FIG. 7. Oölitic chert from Spring Creek. Crossed nicols. $\times 40$.

FIG. 8. Oölitic chert with inclosed fragment of older siliceous oölite layer at right. Crossed nicols. $\times 29$.

limestone, and seems to be the result of lime secretion about algæ. The oölites themselves are small, few attaining a millimeter in diameter. They are usually enlarged by the addition of radiating fibrous calcite, often deposited in several concentric layers. In some of the more perfect spherules the dark interference cross is faintly visible.

FIG. 9.

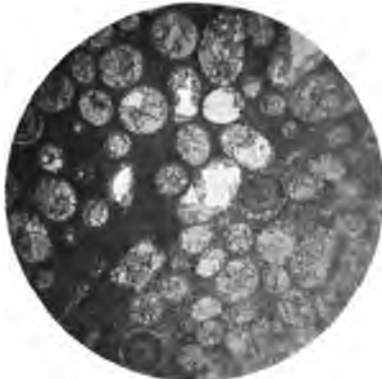


FIG. 10.



FIG. 9. Gray oölitic limestone showing several included quartz oölites. Spring Creek. Crossed nicols. $\times 29$.

FIG. 10. Calcareous oölite near Spring Creek, showing almost complete destruction of oölitic structure due to recrystallization. Spring Creek. Crossed nicols. $\times 29$.

The outer rim and also the nucleus are made up of quartz, showing the same oölitic structure (fig. 12). The oölites are irregular in shape and size, and are made up of concentric layers of fibrous chalcedony about a paler colored irregularly shaped nuclei. In thin sections the color of the oölites is a very pale grayish and translucent yellow, the fibrous structure being indistinct, faintly visible only under the crossed nicols.

FIG. 11.

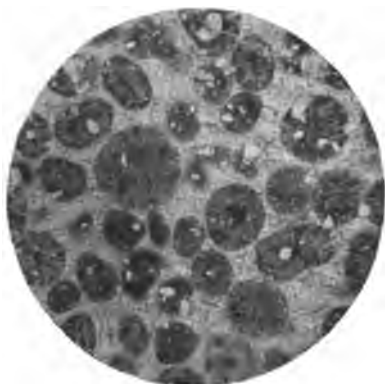


FIG. 12.

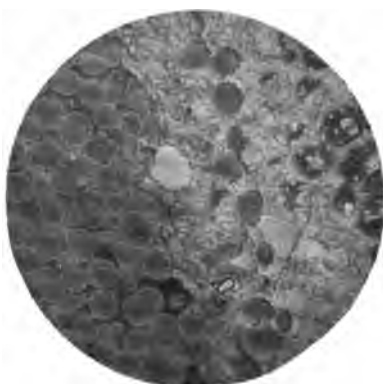


FIG. 13.

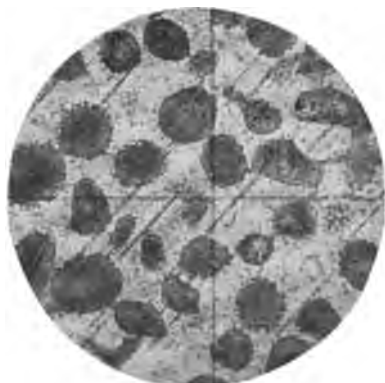


FIG. 11. Oölitic limestone, in which the oölitic chert concretions occur. $\times 40$.

FIG. 12. Outside boundary of the chert nodules, showing the replacement by quartz. $\times 29$.

FIG. 13. Inner crystalline ring, showing partially replaced quartz oölites in large calcite crystal. $\times 50$.

The outside rim of the separate oölites is clear white, transparent, and well-defined fibrous chalcedony. The cementing

material is brownish yellow, weakly translucent, and fibrous quartz. Occasionally small vugs are left whose sides are roughly parallel to the sides of the separate oölites and which have been filled with beautifully colored fibrous chalcedony. The outside margin of the rim is a ragged, irregular line. About an average distance of 0.2^{mm} from the outer edge there is a well defined row of quartz oölites. Two or three tenths of a millimeter on the outer side of this row the oölitic structure of the limestone becomes apparent. Close about the concretion the limestone shows evidences of recrystallization and hence has probably lost its oölitic structure on this account.

The inner crystalline ring (fig. 13) of the concretion proves to be made up of large well-defined calcite crystals showing

FIG. 14.



FIG. 14. Oölitic chert concretions, with inner crystalline ring (A), and chert nucleus (B).

sharp twinning lines, which are penetrated by a dense intergrowth of quartz grains. Many of the quartz grains of this inner ring have a nucleus enlarged by thinly fibrous chalcedony. On account of the dense intergrowing structure of the fibers, the quartz acts as an isotropic mineral, hence is uniformly black throughout a whole revolution of the stage between crossed nicols. In fact, at first, this complete extinction led to the assumption that all the quartz had the same optical orientation. Closer observation disproved this assumption. The separate grains are rounded in general appearance, with their boundaries with the cementing calcite curiously pitted into small angular embayments, which are invaded by the calcite. The latter is in large well-defined grains and over areas up to one and one-half centimeters in diameter has the same optical orientation. It was estimated that one grain of the calcite had from 100 to 270 quartz grains enclosed in it. At both the boundaries with the outer chert layer and the inner nucleus the calcite presents an irregular front with many small points and peninsulas extending out into the quartz. These are always confined to the cementing material. The manner in which the calcite extends into the quartz rims and envelops the separate oölites suggests the spreading of a flood through a district covered with many small rounded elevations.

The Origin of the Oölitic.—Study of the field-occurrence of

the oölites and their relation to the adjacent rocks have convinced the author that no theory of origin will meet all the conditions.

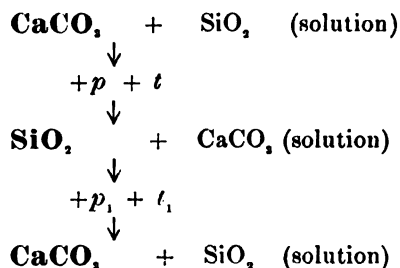
The calcareous oölite so abundant in the Cambrian and Ordovician rocks may be considered to be the result of direct deposition from the lime-bearing ocean water. Most of the older rocks are unfossiliferous and are conglomeratic in character. Thus many of the lower Ordovician limestones are characterized by peculiar conglomerates of flat elongated limestone pebbles, irregularly mixed and shuffled together so as to suggest the name "edge-wise" conglomerate to Stose.* As Rothpletz suggests, most calcareous oölites are the result of concretions of calcium carbonate about algæ.† We may also have direct deposition of calcium carbonate about grains of limestone or quartz along the shore of partly enclosed seas.‡ This seems to be proven by the presence of sand-grain nuclei in most cases, which suggest a deposition about rolling sand. This hypothesis would postulate a shallow water condition for this part of Pennsylvania, an assumption also supported by the many shale partings in the limestone, which are commonly ripple-marked. The prevalence of clastic rocks, such as the edgewise conglomerate, the presence of cross bedding, the rapid alternation in the character of the sediments, all seem to confirm the idea that the sediments were laid down in shallow water, while the occurrence of brachiopods such as *lingulepis*, with their valves filled with oolites, seem to confirm the idea of origin syngenetic with the limestone.

In accounting for the origin of the oölitic concretions described as type four, practically contradictory structures must be taken into account; thus the entire make-up of the quartz ring and nucleus and its analogous structure with the oölitic limestone prove that they are a replacement of the latter. The remarkable resemblance in size, shape, and the nuclei of the oölites are the points in favor of this view. On the other hand, the interior crystalline ring, the lines of contact between this and the quartz, and the latter and the limestone, are points just as strong which proves that calcite has replaced part of the siliceous concretion, finding the cement the less resistant. Thus the reaction apparently proceeded in one direction for a time and then reversed due to a change in the physical or chemical conditions, thus following the law of mass action. We may represent the reactions as follows graphically:

* U. S. G. S., Folio No. 170, and Geol. Mich., vii, p. 66.

† Am. Geol., x, p. 279.

‡ Geikie's Geology, p. 150.



The compounds in the black-faced type represent the solid material and the reactions are entirely physical, depending mainly on temperature and pressure. In this connection it may be interesting to note that the CaCO_3 is more soluble in cold than in hot water,* while the reverse is true for SiO_2 . It is, however, more probable that the reaction depends on a change in the character of the solution. Thus if an alkali solution of SiO_2 be acidified by CO_2 in the presence of CaCO_3 , we get a precipitation of SiO_2 and a solution of CaCO_3 .† Thus:



If the acid solution should again become alkaline the tendency would be for the reaction to proceed in the opposite direction.

There are two theories at present to account for the origin of the bedded oölites. In the first, on the basis of a syngenetic origin they are believed to be the result of deposition by hot springs located on the shore of the Calceiferous sea. As especially important in this connection have been considered the large concretionary bowlders of the chert occurring within the area of the oölite. These bowlders, supposed rims of hot springs and geysers, are not found, however, wherever the oölites occur. Thus none of them were observed with the siliceous oölite along Spring Creek nor slightly east of the area of the accompanying map on Logan Creek. Again in the area of oölite occurrence between Pine Grove and Pine Hall, none occur. Bowlders like those described were found southeast of State College and west of Oak Hall; but no oölite occurs there.

The relation of the oölite to the adjacent rocks seems to furnish the best clue as to their origin. Thus we have at least two distinct methods of origin as exemplified in this area. Figure 7 shows the occurrence of fine-grained and pure sandstone layers interbedded in dense, light gray limestone. The sandstone as a rule is friable and may be crumbled easily by slight

* Comley, "A Dictionary of Chemical Solubilities," p. 82.

† Reactions observed in the Chemical laboratories of the So. Dak. State School of Mines by Prof. Coolbaugh.

pressure. A few of the layers are highly cemented and form quartzite. These show secondary enlargement in many cases and a cement of fibrous chalcedony. Angular fragments of limestone are often included in the sandstone layers and seams, and cracks in the limestone are often filled with the sand. The character of these cracks shows that they were joint cracks formed subsequent to the hardening of the limestone, and that at this time the sandstone was not yet cemented, and hence was squeezed into these cracks to form the miniature dikes. Subsequent to their formation silica-laden water percolated through these rocks, finding their readiest passage in the porous sandstone, at the same time depositing their silica about the quartz grains and forming the layers of siliceous oölite. As is evident in the case of the Krumrine oölite, calcareous oölites were also replaced by silica to some extent, probably by the same solutions which formed the siliceous oölite on Spring Creek, and a comparison with fig. 6 will show the close analogy between them. In order to have perfect oölites, such as are present in these rocks, a certain amount of free motion is usually considered requisite, which would of course be a factor opposing the above assumption. If we assume, however, that some of the sandstone consisted of grains already concentrically enlarged, shifted back and forth by water currents, and then deposited in layers with the limestone, we overcome this obstacle. Subsequent to their deposition in strata the final cementing of the oölitic spherules took place. Many of the oölite layers have enclosed in them angular fragments of different oölites (see figs. 3 and 8), also pebbles of limestone, and frequently chert nodules. That contemporaneous erosion was active, and that this was a period of oscillations between the land and the sea, has already been shown. The solutions were in all probability hot springs, as Wieland claims, and were located on the shore of the Calciferous sea. The retreats of the sea gave the opportunity for the hot, silica-laden waters to replace some of the layers of oölitic limestone, but what is more important, to form by direct deposition about the sand grains the siliceous oölites. As a result of the unstable coast line some of the oölite layers were eroded and their fragments were re-deposited in some cases in lime-muds, in other cases in other oölite horizons. Siliceous spherules of oölite also occur through many of the associated limestones and so strengthen this view.

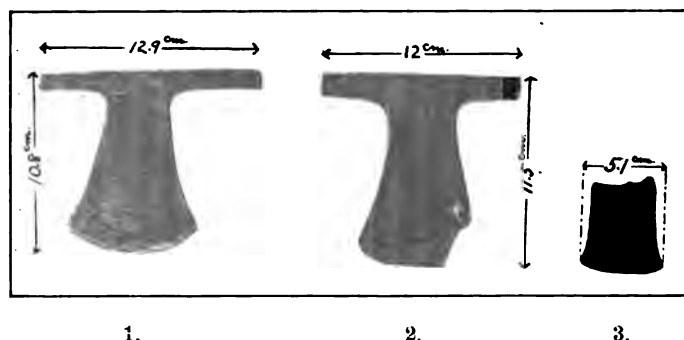
Summary.—In conclusion, then, it may be said that siliceous oölite occurs predominantly in rocks of Upper Cambrian and Beekmantown age; that there is a series of definite layers, a conservative estimate being at least twenty; that some of the layers are the result of replacement of oölitic limestones, but that the majority are the result of direct deposition of silica from hot solutions about pure quartz sand.

ART. XII.—*The Composition, Structure, and Hardness of Some Peruvian Bronze Axes*; by H. W. FOOTE and W. H. BUELL.

DURING the summer of 1911, Prof. Hiram Bingham, while with the Yale Peruvian expedition in eastern Peru, obtained three bronze axes which appear to belong to the Inca period. These axes were turned over to the authors and form the basis of the present investigation.

In the photograph of the axes, fig. 1, we have numbered the specimens and given the dimensions. Nos. 1 and 3 were

FIG. 1.



found on the site of an old Inca settlement near the Pampaconas River in latitude $12^{\circ} 30' S.$ and longitude 73° . This river has not yet been mapped. It is a western branch of the Urubamba River, flowing nearly parallel and emptying into it at some point below Icharate. The settlement where these axes were found had been entirely deserted and all the original clearings were covered with forest. A few years ago, a small tract was cleared and it was in this new clearing that the axes were found. Axe No. 2 was found in the valley of the Urubamba River near Rosalina.

In our investigation, we have determined, first, the chemical composition of the axes; second, their micrographic structure, and third, their hardness. By comparing the structure of one of the axes with that of a new alloy of the same composition, we have been able to draw conclusions as to the methods used originally in making the axes.

The following results were obtained on analysis:

	No. 1	No. 2	No. 3
Tin	12.03	5.58	3.36
Copper	88.06	93.94	96.44
Iron	0.08	none	trace
Silver	none	0.65	none
Sulphur	0.35	0.08	0.23
Lead	none	trace	none
	<hr/> 100.52	<hr/> 100.25	<hr/> 100.03

The results show that the alloys are all bronzes which vary considerably in their percentage of tin and contain a small amount of sulphur. No. 2 also contains silver in small amount.

The alloys of copper and tin have been most thoroughly investigated by Heycock and Neville* and by Shepherd and Brough.† Their results show that alloys containing not more than approximately 10 per cent of tin consist entirely of a solid solution of tin in copper, stable at all temperatures below the melting point, and made up of so-called α -crystals. Alloys containing between 10 and 22 per cent of tin deposit on solidifying a mixture of α - and β -crystals. The β -crystals consist also of a solid solution of the two metals but contain more tin than the α modification. They are stable only above 480° C. and if cooled slowly below this transition temperature, δ -crystals are formed. These are extremely brittle and an alloy containing them cannot be successfully worked either hot or cold. If, however, the alloy is quenched rapidly from a temperature above 480° C., a mixture of α - and β -crystals results which is characterized by great strength and tenacity. This alloy can be forged. It is evident, therefore, that the properties of an alloy whose composition is between the limits mentioned above, depend very largely on its previous heat treatment, since the properties of β - and δ -crystals are different.

Referring to the analyses of the bronzes, No. 1 appeared to be the most interesting from a metallurgical standpoint, containing, as it does, 12 per cent of tin, or enough to yield either β - or δ -crystals. For comparison, a bar of metal was cast of nearly the same composition as this axe. It contained :

Tin	12 per cent
Copper	88 "

From this bar an axe was forged which we shall call the "new axe." In forging the new axe, we endeavored first to work it hot without paying much attention to the temperature, but found this could only be done above 500° C. After heating followed by slow cooling, the alloy was still extremely brittle.

* Phil. Trans., ccii A, 1, 1903.

† Jour. Phys. Chem., x, 630, 1906.

Under a hammer, it broke in pieces. By heating above 500° C. and quenching, however, to retain the β -crystals, we were able to forge the axe cold without any material difficulty, but it was found necessary to anneal at intervals during the forging, heating each time above 500° C. and quenching.

Photographs were made showing the microstructure of the original casting from which the new axe was made, before the alloy had been worked or annealed. Fig. 2 shows this structure, which is characteristic of alloys of this type, made up of fern-like or kidney-shaped 'casting crystals.' Figs. 3 and 4 show the structure of the new axe in its finished condition after annealing and forging as described above. Fig. 3 was taken near the center of the axe and shows the crystals with no distortion. Fig. 4 was taken near the edge and shows slight distortion of the crystals due to forging. From a comparison of figs. 2, 3, and 4, it is evident that the structure has been entirely changed by annealing and forging.

The original axe, No. 1, shows from its shape, and from the

FIG. 2.



FIG. 3.



FIG. 2. Showing casting structure of new axe.

FIG. 3. Showing structure on center of finished axe. Made from metal shown in fig. 2.

marks on it, that it has been forged. The original shape of the casting cannot be told, but there can be no doubt that the shape has been materially changed by the forging. Figs. 5 and 6 show the micro-structure of this axe. It is similar in type to that shown in figs. 3 and 4 and entirely different from that in fig. 2. The size of the crystals is different. That, however, is controlled by the temperature before quenching. The size of crystals produced by annealing is usually a

FIG. 4.



FIG. 5.



FIG. 4. Showing structure on edge of new axe. Made from metal shown in fig. 2. Crystals somewhat distorted due to hammering.

FIG. 5. Showing crystals near edge on axe No. 1. The structure of the metal was poor and it was impossible to get a very good etching.

function of the temperature and the size can be increased by raising the temperature. The time of heating is not important except at low temperatures or when the heating has been continued for a long time, for example, for several days.

FIG. 6.



FIG. 7.



FIG. 6. Showing crystals in center of axe No. 1. The structure of the metal was poor and it was impossible to get a very good etching.

FIG. 7. Showing fine crystals, which occur only at one point of edge on axe No. 3.

Taking into account the facts of micro-structure and that the axe has been forged, it is fair to infer that after casting the original alloy, it was heated to a temperature considerably above 500° and either forged hot or quenched suddenly and forged cold. This required a very considerable degree of skill on the part of the original makers.

FIG. 8.



FIG. 8. Showing crystals on axe No. 3, a short distance from edge on cross section.

We were unable to obtain an etching of axe No. 2. Apparently the silver in it gave trouble by dissolving in all the etching solutions which we tried and reprecipitating on the surface, leaving a dark deposit which prevented the microstructure from being observed. Figs. 7 and 8 show the microstructure of the fragment of axe No. 3. Both views were taken on the broken section. The fine crystals occurred close to the edge at the extreme left as shown in fig. 1 and the coarse crystals occurred nearer the center. The axe was therefore very unevenly heated, either in the original annealing or at some time afterward.

None of the old axes are very hard. The following table gives the results of the scleroscope tests:

	New axe	No. 1	No. 2	No. 3
Edge.....	36	26	18	18
Center.....	34	24	20	..

The hardness was taken with the Shore scleroscope and it varies somewhat with the percentage of tin as would be expected, but shows nothing at all unusual. In fact, the hardness of the old axes is considerably less than that of the new axe, which is probably due to coarser structure as well as to composition. The values given in the table are expressed in empirical units and merely give comparative values among themselves. For the sake of comparing the hardness of the axes with that of another metal, it may be well to add that a piece of cast brass has a hardness on the same scale of 11 or 12 units.

Chemical Laboratories of the Sheffield Scientific School
and of the Winchester Repeating Arms Co.
New Haven, Conn., May, 1912.

ART. XIII.—*The Photoelectric Effect of Phosphorescent Material*; by CHESTER A. BUTMAN.*

THE first work done on the photoelectric effect of phosphorescent materials was that of Elster and Geitel.† Other workers are G. C. Schmidt,‡ P. Lenard and Sem Saeland,§ and Maryan Grotowski.¶ The following facts asserted by Lenard and Saeland were confirmed by me, for CaBiNa, the most strongly photoelectric substance used by them.

(A) The photoelectric effect stops the moment the light is shut off.

(B) Light which does not produce phosphorescence does not produce the photoelectric effect.

(C) If red is added to a color causing phosphorescence, it has no influence on the magnitude of the photoelectric effect.

In addition to the foregoing, the velocities of the electrons, ejected when the material is exposed to light which has passed through glass, have been carefully determined. In order to gain more knowledge about the velocities, it was found necessary to make a study of the photoelectric fatigue of this material. This fatigue in this case is different from the photoelectric fatigue of metals, in that it takes place in a high vacuum and recovers after a lapse of time when not exposed to the light.

The source of light adopted was the carbon arc which was run at 10 amperes and 65 or 70 volts. This provided a light of constant intensity as was shown by being able to repeat readings exactly. The light which fell on the material passed through a glass condensing lens.

The electrometer was of the Dolezalek type, used with a quartz fiber suspension. The needle was charged with 80 volts every day. The sensitiveness was about 1,500 millimeters per volt with the scale about 70^{cm} distant. The deflections were of the same magnitude along all parts of the scale.

The highest vacuum used was .00001^{mm} of Hg as recorded by the McLeod gauge; the lowest, .03^{mm}. The vacuum was maintained constant by running a Gaede pump to take up any small leak. Tests were made of the photoelectric effect at dif-

* See also abstract of article read before the American Physical Society, Dec. 30, 1911, *Physical Review*, p. 158, 1912.

† J. Elster and H. Geitel, *Ann. Phys.*, xxxviii, 508, 1889; xlv, 722-736, 1891.

‡ G. C. Schmidt, *Ann. Phys.*, lxiv, 708-724, 1898.

§ P. Lenard and Sem Saeland, *Ann. Phys.*, xxviii, 476-502, 1909.

¶ Maryan Grotowski, Thèse l'Université de Fribourg, Librairie de Jules Roussel, Paris, 1910.

ferent pressures and it was found that with any vacuum better than $\cdot 1^{\text{mm}}$ the maximum effect was obtained.

The apparatus (fig. 1) consisted of a brass tube (B) closed at one end by a quartz plate (C) and at the other by a vulcanite cap (O). The cap was removable by melting the wax which held it in place. (A) is a brass tube on which was fitted a glass tube which led to a McLeod gauge and from thence to a Gaede vacuum pump. (Q) is a brass wire net one inch from

FIG. 1.

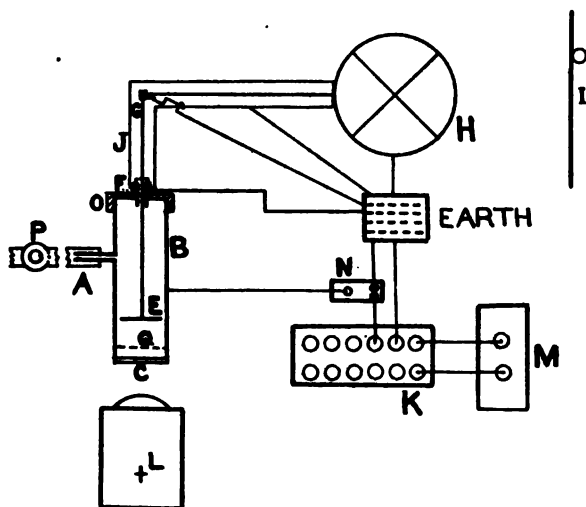


plate (E). (E) is a brass circular plate on which the phosphorescent material was mounted. This plate was supported by a brass rod which ran through an amber plug in the vulcanite cap, being surrounded by a brass guard tube (F). The rod went as far as (G), where it was soldered on to a rod connecting it with the Dolezalek electrometer (H). The electrometer and plate could be grounded by means of a connection at (G). (J) is a brass tube surrounding the rod.

A potentiometer (K) could be connected to the case (B) by means of a switch at (N). (M) is the battery. Thus by reversing the connections accelerating and retarding fields could be put on the case. (I) is the lamp and scale for the electrometer. (L) is the source of light. A phosphorous pentoxide bulb was placed at (P) to absorb the moisture.

Method of Experiment.

The phosphorescent material to be examined was ground to a fine powder with alcohol in an agate mortar. The coarse

particles were allowed to settle out and then the fine particles were permitted to deposit themselves on a metallic plate which could be fitted over the brass plate in the tube. This method gave a uniform layer of any desired thickness which would remain on the plate. Plates of platinum and lead were used to place the material upon.

The substances experimented with were Sidot Blende (ZnS) prepared by the Braunschweiger Cheminfabrik—phosphorescent light yellow, and calcium sulphide prepared by myself after the method of Lenard and Klatt (5).^{*} The composition was 2g. CaS, 0.1g. Na₂SO₄, 0.05g. Na₂B₄O₇, 0.05g. CaF₂, 0.00048g. Bi. Chemically pure materials were used with the exception of the calcium fluorite, which was the ordinary fluorite. The bismuth was introduced in the form of an oxide. The calcium sulphide was prepared by heating some carbonate until the CO₂ gas was driven off. Two grams of the CaO were mixed with 1.35 grams of powdered stick sulphur and heated in a covered porcelain crucible over a Bunsen burner. The CaS was then placed in a mortar and mixed with the other materials. The whole mass was then put in a crucible and heated strongly over a blast flame for twenty minutes. This material is called by Lenard CaBiNa. The color of the phosphorescent light is blue.

The apparatus used is very convenient, since no effect can come from anything except the material under investigation, and as no metals (with the exception of Na, K, Rb and certain alloys) give any photoelectric effect after the light has been passed through glass. Glass cuts off rays shorter than about 3200 Ångström. Tests were made with voltages ranging from 0 to ± 600 volts on the case, and with Pt and Pb plates, but no effect was ever obtained except when phosphorescent material was on the plate. Hence, I was able to use a layer of material so thin that it consisted of discrete particles.

Photoelectric Fatigue and Recovery of Phosphorescent Material.

An examination of the curves for photoelectric fatigue obtained will show that there is a rapid drop from the initial value to a value that is nearly constant for several hours. Hence, by waiting until this steady photoelectric state is reached, comparative results may be readily obtained.

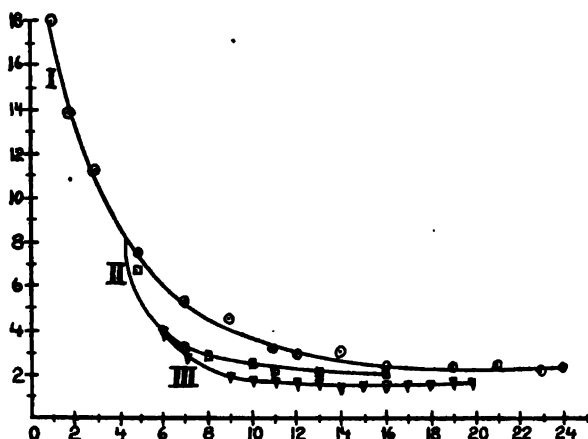
It will also be observed from the curves that the values of the deflections are less for each of three successive days. The curves are placed as to render comparison easy. They represent the number of centimeters deflection in successive one-half minute periods. The phosphorescent material was

^{*} Lenard and Klatt, *Ann. Phys.*, xv, 425, 1904.

Ca,Bi,Na. The vacuum varied between $\cdot 0007$ and $\cdot 002^{\text{mm}}$. The sensitiveness of the electrometer during this test was between $1600\text{--}1700^{\text{mm}}$ per volt. The accelerating field used was 2 volts. Curves I and II were run with a wait of two and one-half minutes with light off between readings. The electrometer was grounded and allowed to return to zero during the wait. Curve III is a set of continuous readings.

Another important feature is the *recovery* from fatigue during the night. The recovery is less on successive days.

FIG. 2.



Between I and II no field was on the case during the night. Between II and III a voltage of two volts was on the case.

Experiments were made to see what effect the thickness of the layer had on the photoelectric fatigue. No matter how thick or thin the layer was, fatigue and recovery were always present. A moderately thick layer was measured and found to be $\cdot 06^{\text{mm}}$. The thinnest layer examined consisted of discrete particles with large distances between them.

A series of experiments were performed to find out the influence of voltage on fatigue. With positive 600 volts on the case the fatigue was found faster than with two volts. It was found, for instance, that a constant value of deflection could be obtained for two volts. Now if higher voltages up to 600 volts were put on the case and a series of readings taken, it was always found that the reading with two volts was much less than it had been before and in some cases no deflection at all could be obtained. If now the maximum voltage of 600 volts was put on the case approximately the same value as before was obtained.

The material was found to fatigue irrespective of the field, when the light was on the substance. Fatigue occurred with no field on and with positive or negative voltages up to 600. It is important to notice that *no deflection* was ever obtained when using *negative* fields on the case ranging from 2 to 600 volts; however, if the light was on, the material fatigued, as was demonstrated by taking a reading with no field before and after exposure.

The foregoing experiments were all made on CaBiNa. No particular study was made of the photoelectric fatigue of Sidot Blende, but in general it showed the same properties of fatigue and recovery as exhibited by the CaBiNa.

The results of these experiments may be summed up by saying that the following hold when the plate is insulated:

1. When there is light there is fatigue.
2. When there is no light, there is recovery.
3. High positive voltages accelerate fatigue, with light.
4. Photoelectric fatigue and recovery is an inherent property of phosphorescent material.
5. The photoelectric fatigue is due solely to the incident light.

Velocity of Electrons from Phosphorescent Substances.

It was found that the velocities of the electrons depended on the state of the material. There are three states, (1) the electrons have a velocity, (2) they have no velocity, (3) they require an attracting field in order that any may leave the substance. These three states probably merge one into the other as the material fatigues. The highest observed potential necessary to prevent the electrons from leaving the CaBiNa was -0.35 of a volt. The field necessary to get any effect at times was more than $+4$ volts. However, by applying a strong enough assisting field I was always able to get an effect.

The highest negative field necessary to keep the electrons coming off from the Sidot Blende was -0.75 of a volt.

Another important fact should be noted, and that is that the saturation values change with the state of fatigue. For instance, the following results were obtained with CaBiNa, taking the field as a measure of the velocity:

Velocity	-0.35	corresponded to	saturation value	$+0.25$
"	± 0.0	"	"	$+0.5$
"	$+ .3$	"	"	$+1.0$

However, these saturation values appear to hold only for voltages between 0 to about 40 volts. Curves drawn from a number of sets of reading would seem to indicate that complete saturation would be obtained at 800 volts. A typical set

of readings is given below. The fatiguing effect due to high voltages will be readily noted. The vacuum was $\cdot 008^{\text{mm}}$.

Field	Cms. per half min. increasing field to 600	Cms. per half min. decreasing field from 600
— 0·35	0	--
0·0	1·0	0·4
+ 0·3	5·1	--
+ 2·0	5·0	2·0
40·0	--	5·4
80·0	--	6·0
120·0	--	6·5
160·0	--	6·5
200·00	7·6	7·0
400·00	7·8	--
600·00	8·0	--

Action of Different Parts of the Spectrum.

Light through green, yellow, and red glass gave no photoelectric effect and did not excite phosphorescence. The light transmitted by these glasses was measured with a Hilger wavelength spectrometer. From these data it was seen that the photoelectric effect stopped at 4100 \AA . for CaBiNa. Sidot Blende gave no effect with red glass and was not excited by red, yellow or green light. The extreme red transmitted as shown by the spectrometer was 7450 \AA .

Experiments were made with infra-red light, but no effect whatever could be obtained. Voltages from 0 to ± 600 volts were used on the case. The infra-red light was obtained by interposing a thin sheet of vulcanite between an open arc and the quartz window of the chamber.

Some experiments were made with light that had passed through blue Uviol glass and the effect was obtained. If light of all wave lengths from an open arc was used the deflection was larger, but the effects were of the same character as observed when the light was passed through glass. My experiments were made through glass, thus eliminating the problem of reflected light on the case.

Discussion of Results.

In order to explain the phenomena observed, the hypothesis may be made that the electrons set free get entangled in the substance and build up fields in it. Fatigue would then be due to this accumulated field building up. A strong field on the case would overcome the field in the substance so that an effect could be obtained. It must be remembered that these phosphorescent substances are good insulators of the order of quartz. Hence, this accumulated field is not neutralized when the plate is earthed. Recovery would seem to be due to the

recombination of the electrons, which probably takes place quite slowly.

The acceleration of fatigue with the higher voltages is probably due to the larger amounts of negative electricity taken away, leaving the corresponding positive charge with less negative charge to counteract it.

Experiments were made on the components of CaBiNa to see if the element which caused the photoelectric effect could be determined so that its properties could be studied without any complications. Thus it was discovered that sulphur gave a photoelectric effect with light longer than 3200 \AA . This was the only one of the components which gave such an effect. Hence, the hypothesis was advanced that the photoelectric effect of the phosphorescent alkaline earth sulphides is due to the sulphur they contain. Experiments are being conducted to test this theory.

Before concluding, the author wishes to express his thanks to Professor Bumstead, at whose suggestion this investigation was undertaken, for his interest in the work, and to Professor Boltwood for many valuable suggestions.

Conclusions.

1. Photoelectric fatigue and recovery is an inherent property of the material and is due solely to the incident light.
2. High positive voltages accelerate fatigue with light.
3. The velocities of the electrons ejected are dependent on the photoelectric state of the material.
4. The saturation value is dependent on the photoelectric state of the material.
5. No photoelectric effect can be obtained with CaBiNa with a wave length longer than about 4100 \AA .
6. Sulphur is photoelectric with lights of a longer wave length than 3200 \AA .

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NOTE.

In further support of the theory advanced here may be cited the fact recently discovered by the author that sulphur is actinodielectric in addition to being photoelectric.* With the apparatus arranged to test for the actinodielectric effect it was found that with *red* glass cutting off wave lengths shorter than 6000 \AA ., and with white light through glass, that a deflection was obtained *in the direction of the applied field*. The field used was about 100 volts. Further experiments are in progress.

Amherst, Mass., May 24, 1912.

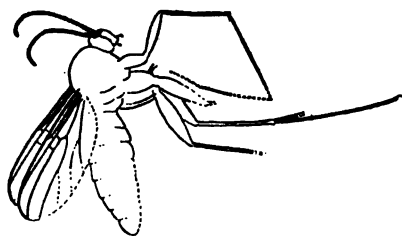
*See Ann. der. Phys., pp. 445-454, 1911, "Über die aktinodielektrische Wirkung bei den Erdalkaliphosphoren, nach Versuchen von Rob. Oeder, von C. Ramsauer und W. Hausser.

ART. XIV.—*A Tertiary Fungus Gnat*; by O. A.
JOHANNSEN.

THROUGH the kindness of Professor T. D. A. Cockerell I have had the privilege of examining a species of *Mycomya* (*Sciophila* Winnertz) from the Miocene shales, Florissant, Colorado. As it is unnamed and quite well preserved I take pleasure in describing it.

Mycomya cockerelli n. sp. (Diptera: Mycetophilidæ.)
Male. Length, 5^{mm}; abdomen, 3·5^{mm}; wing, 3·5^{mm}. Head, thorax, abdomen, and femora pale reddish brown; the vertex, the vitta (or vittæ) on mesonotum, some spots on the pleura, the sternum, metanotum, the hind margins of the abdominal segments, the tibiæ and tarsi, darker brown. Middle coxæ

FIG. 1.



apparently with anterior spurs; fore metatarsus about 1·3 times as long as the tibia; wings about 1·5 times as long as the fore metatarsus, the veins brownish; the subcosta ends about opposite the middle of the small cell R_1 , the subcostal crossvein (Sc_1) on the proximal third of this cell; cell R_1 about twice as long as wide. The origin of M_1 and Cu_1 cannot be clearly distinguished. Judging from the course of M_1 , M_1 arises at a point about midway between the base of the petiole of M and the tip of M_1 ; Cu_1 apparently arises about opposite the base of the $R-M$ crossvein.

The accompanying camera lucida figure is enlarged about five times. The dotted lines indicate conjectural structure. Holotype in the Peabody Museum (Yale).

Maine Agricultural Experiment Station,
Orono, Maine.

ART. XV.—*Heat of Formation of the Oxides of Vanadium and Uranium, and Eighth Paper on Heat of Combination of Acidic Oxides with Sodium Oxide; by W. G. MIXTER.*

[Contributions from the Sheffield Chemical Laboratory of Yale University.]

THE determination of the heat of formation of the oxides of vanadium is simple calorimetric work provided the pure metal in the form of a fine powder is available. This has not been obtained and the results only show that the heat of oxidation is very high.

Vanadium.

Roscoe obtained fairly pure metallic vanadium in small quantities by reducing the chloride with hydrogen; Moissan reduced the oxide by carbon in the electric furnace and the product contained several per cent of carbon. Other methods have been tried, but, with possibly one exception mentioned later, have yielded only impure metal. One specimen purchased for electrolytic vanadium contains only 85 per cent of the metal, and another marked "fused, c. p." 82 per cent. Both specimens contain carbon. Weiss and Aichel* reduced vanadium pentoxide with the mixed cerium metals and obtained a fused metallic product which was brittle and scratched quartz. For analysis they converted 0.2062 gram of it into vanadyl sulphate, and made the solution to 500^{cc}. They titrated 20^{cc} of this solution containing 0.0082 gram and obtained 0.0082 gram of vanadium. It is doubtful if an analysis made with so small quantity gives an accurate result. The writer has used for the determination of vanadium the old method as follows: 0.2 to 0.5 gram of the metal or oxide is dissolved in nitric acid and the solution evaporated to dryness in a weighed platinum crucible, then heated slowly in an electric furnace to a temperature a little under the melting point of vanadium pentoxide. The heating was repeated until a constant weight was obtained. It was found that wetting the residue with nitric acid, drying and heating again, did not increase the weight. A test of the method was made by treating 0.5740 gram of vanadium pentoxide with nitric acid. The weight was unchanged. The method presupposes either the absence of substances that will leave a residue by the treatment or the determination of them.

It was found that magnesium and an oxide of vanadium react violently when heated. With the hope of obtaining the metal in a powder or a lower oxide the following was carried

* Liebig's Ann., cccxxvii, 380.

out. An intimate mixture of 23 grams of vanadium pentoxide and 19 grams of magnesium powder was heated in a heavy brass bomb. At a temperature below redness the reaction occurred and the bomb became red hot. The porous brown product was digested with a solution of ammonium chloride which dissolved the metallic magnesium present but not the vanadate or vanadite. The product was next washed, dried, pulverized and then repeatedly digested with very dilute hydrochloric acid and finally with acid diluted with two volumes of water. The product at this stage consisted of grains having a metallic luster and a brown powder. The latter was floated off and the residue was washed and then dried in a partial vacuum over sulphuric acid. It was a mixture of bright metallic-like particles and a grey powder. It was slowly acted on by hot concentrated hydrochloric acid with evolution of gas, but was not completely dissolved. It was marked "A" and analyzed with the following results:

	I	II	Mean.
Vanadium	90.1	90.0	90.0
Magnesium oxide	1.44	1.49	1.5
Oxygen by difference			(8.5)

The atomic ratio of the vanadium to the oxygen is 3.3 to 1.

Next a mixture of 38 grams of vanadium trioxide and 22 grams of magnesium was heated in a steel bomb and kept at a cherry red heat for some time. Then the bomb was cooled under water to prevent oxidation of its contents. The product was digested with hot concentrated hydrochloric acid, washed once and then left for a day in dilute acid. It was finally washed and dried as usual. The product was 18 grams and it was found to contain 85.2 per cent of vanadium. It was treated again with hot concentrated hydrochloric acid and considerable hydrogen was evolved. The residue was finally washed with alcohol and dried in a partial vacuum. It weighed 12 grams and was marked "B". An analysis gave 84.5 per cent of vanadium and 0.2 per cent of magnesium oxide. After standing two weeks the vanadium was found to be 83.4. Vanadium monoxide, V_2O , contains 86.4 per cent of the metal.

Another preparation, marked "C," was made in the same way as the 18 grams above described, and contained 89.7 per cent of vanadium. It was a dark gray powder showing no metallic particles under a magnifying glass. The metal reduced by magnesium is in an exceedingly fine powder which settles slowly in water and in the best condition to oxidize. The oxidized product, however, appears to be a mixture, for it

is partially soluble in hydrochloric acid, with evolution of a gas, doubtless hydrogen.

The following determinations were made with the preparations marked "A," containing 90.0 per cent of vanadium and 8.5 per cent of oxygen.

Experiment 1.—"A" 1.000, sulphur 1.000, sodium peroxide 15 grams. Heat effect 9003°. Deducting 5270° for sulphur and 30° for iron burned, and 71° for oxygen absorbed, leaves 3632° for the heat effect of 1 gram of impure vanadium reacting with sodium peroxide.

Experiment 2.—Made as Exp. 1, only 1.200 gram of "A" was taken. Result for 1 gram, 3721°.

The combustions were apparently complete since the fusions left no unburned particles when dissolved in water. The mean of the results is 3677°. This number divided by 0.9, the amount of vanadium in 1 gram, gives 4086° and for the heat of reaction of 102 grams of vanadium, two gram atoms, with sodium peroxide 416,800°. From this number is derived $2V + 5O = V_2O_5 + 348,000^\circ$. If correction be made for the oxygen in the metal used, taking the heat effect of one atom as 145,000°, the result is 422,000°. Preparation "B" in one experiment, making the same correction, gave 460,000°. The average of the last two is 441,000°.

Roscoe* states that vanadium monoxide, V_2O , is formed by the prolonged exposure of finely divided vanadium to the air, but says nothing of its properties except that it is a brown powder. He also states that vanadium is not attacked by hydrochloric acid. The writer has found that all of the preparations made by reducing an oxide with magnesium set free hydrogen when treated with hydrochloric acid, yield a green solution and leave a grey residue which does not dissolve on long heating to 100° in concentrated acid in a sealed tube. The evolution of hydrogen is apparently not due to the action of metallic vanadium on the acid but to the monoxide or dioxide reacting to form V_2Cl_3 (unknown) or VCl_3 , either of which would set free hydrogen from hydrochloric acid. Roscoe states† that when hydrochloric acid is added to a violet solution of vanadium dichloride hydrogen is evolved and the trichloride is formed.

Vanadium Pentoxide.

Vanadium pentoxide was made in the usual way by heating ammonium vanadate. Thus prepared it is commonly regarded as amorphous but under the microscope it appears to be crystalline. It may be that the form of the crystals of ammonium vanadate is not changed on heating and that the

* A Treatise on Chemistry, Roscoe & Schorlemmer, 4th ed., ii, 902.

† Ibid., p. 909.

interstices are invisible. The preparation designated as "D" was fairly pure as shown by the following: 10.413 grams lost on heating to faint redness in hydrogen 1.8300 gram or 17.61 per cent, the calculated loss being 17.58 per cent when V_2O_5 is changed to V_2O_3 . The vanadium trioxide obtained in the experiment is designated as "F". A portion of "D" was fused in a platinum dish and the red crystalline sample obtained was marked "E".

The calorimetric experiments 3 and 4 were made with the yellowish-brown so-called amorphous sample "D", and 5 and 6 with red crystalline portion "E". The following are the data and results:

	3	4	5	6
Vanadate pentoxide.....	5.201	5.062	5.173	5.090 grs.
Sulphur	1.000	1.000	1.000	1.000 "
Sodium peroxide	16.	16.	16.	16. "
Water equivalent of system	3075	3118	3087	3118 "
Temperature interval	3.190°	3.104°	3.185°	3.116°
Heat effect	9809°	9678°	9832°	9716°
" " of sulphur	-5270	-5270	-5290	-5270
" " of oxygen evolved	+176	+176	+175	+177
	4715	4584	4737	4623
" " of 1 gram of V_2O_5	907°	906°	911°	908°

It was found in Exp. 4 that the connections for collecting the oxygen evolved leaked, hence the same correction is made in 3 and 4 as for 4 and 5, as the conditions were essentially alike in all of the experiments. It appears from the results that the so-called amorphous form of vanadium pentoxide is crystalline, for if it is amorphous the heat effect should be higher than that of the red crystalline form. The average of the last two experiments is 910°. For 1 gram molecule of vanadium pentoxide combining with sodium oxide it is 165,000°.

Vanadium Trioxide.

Vanadium trioxide, preparation "F", was used in the following experiments:

	7	8
Vanadium trioxide.....	3.121	3.325 grams.
Sulphur.....	1.000	1.000 "
Sodium peroxide.....	16.	19. "
Water equivalent of system	3056	3134 "
Temperature interval.....	3.225°	3.197°
Heat effect	9856°	10019°
" " of sulphur.....	-5270	-5270
" " " oxygen absorbed..	- 51	- 59
	4535	4690
" " " 1 gram of V_2O_3 ..	1453°	1411°

The average, 1,432°, multiplied by 150 equals 214,800° for the heat of the reaction of 1 gram molecule of vanadium trioxide with sodium peroxide.

Experiment 9.—The direct determination of the heat of oxidation of vanadium trioxide was made by the method used for finding the heat of combustion of titanium*; 3 grams of "F" were used. It was not completely changed to V_2O_5 . A weighed portion of the combustion product was oxidized by nitric acid and the vanadium in it determined. From the data obtained the atomic ratio of the vanadium to the oxygen was found to be 1 to 2.2. The heat effect observed in the calorimetric experiment is 1664°, that due to the cotton taken 558°, leaving 1104°. Hence $1104 \div 3 \times 150 = 55,200^\circ$ for the effect of 1 gram molecule of vanadium trioxide burning to form the tetroxide and some pentoxide.

Vanadium Tetroxide.

Vanadium tetroxide was made by heating to redness for half an hour in an exhausted tube a mixture of equivalent quantities of the tri- and pentoxide. The tube swelled some, showing that oxygen was given off in small quantity. The product was a coke-like mass. An analysis of it gave 61.1 per cent of vanadium; calculated 61.1 for V_2O_4 . Vanadium tetroxide burns readily with sodium dioxide without addition of sulphur to the mixture. Two determinations in each of which 4 grams were used gave respectively 1084° and 1021°. The mean is 1052° or 174,600° for the reaction of one gram molecule of vanadium tetroxide reacting with sodium dioxide.

Vanadium Dioxide.

Vanadium dioxide has been obtained in crystals by reducing vanadium oxychloride, $VOCl$, with hydrogen. Berzelius† heated a mixture of vanadium pentoxide and potassium, removed the soluble portion with water and regarded the product as a metallic vanadium. Roscoe‡ says it was a mixture of oxides, and also§ that it was the dioxide. It is commonly stated in the literature that vanadium dioxide may be made by the method of Berzelius. It does not appear, however, to have been further investigated. Roscoe|| heated vanadium pentoxide and sodium in a closed iron crucible, washed the product and obtained vanadium trioxide mixed with a little higher oxide. The writer attempted the reduction with

* This Journal, xxxiii, 45.

† Pogg. Ann., xxii, 3.

‡ Phil. Trans., clix, 687.

§ Ibid, p. 690.

|| Roscoe and Schorlemmer's Treatise on Chemistry, 4th ed., ii, p. 903.

sodium as follows: 25 grams of vanadium trioxide and 15 grams of sodium were heated in a heavy brass cylinder closed with a screw plug. The reaction was very violent and the plug was partly melted. The metallic sodium remaining was removed by alcohol and the residue left was washed with water, alcohol and ether and dried *in vacuo*. It weighed 15 grams. Next, this 15 grams and sodium were heated in an iron cylinder until sodium nearly ceased to burn about the screw cap. On opening the cold cylinder the contents ignited on top and it was at once placed in alcohol. But little hydrogen came off. The black powder obtained was washed with water, digested with dilute hot hydrochloric acid which dissolved some of it, and finally washed with water and dried. It was found on analysis to be almost pure vanadium trioxide. Undoubtedly sodium reduces vanadium trioxide, but is not as well adapted for the reduction as potassium, which does not react as violently probably because the latter metal distills at a lower temperature than sodium.

The following preparations were made in an iron cylinder of little greater capacity than the bulk of the mixture. Potassium was placed in the bottom of the cylinder and vanadium trioxide in a bulky powder on top except in one case mentioned later. The cylinder was kept at a red heat until potassium ceased to burn about the screw cap, and then quickly cooled in water. The black product was digested and washed with cold water and dried *in vacuo* over sulphuric acid. A weighed portion of the product was converted into the pentoxide for the determination of the vanadium.

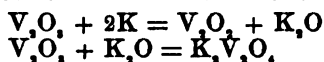
Preparation "H."—7 grams of vanadium trioxide and 5 grams of potassium. Product, 2 grams, containing 75.9 per cent of vanadium; V_2O_5 has 76.1 per cent.

Preparation "I."—Vanadium trioxide, 12 grams pressed down in the cylinder, potassium 7 grams; yield 7 grams. Vanadium content 72.5 per cent. Equal molecules of V_2O_5 and V_2O_3 contain 72.1 per cent. A determination of the heat of reaction of "I" with sodium peroxide showed that the oxides were not combined.

Preparation "J."—25 grams vanadium trioxide and 15 grams of potassium. The cylinder unfortunately was imperfect and opened when cooled under water and the product was mixed with iron scale. The black powder which was separated from it by floating yielded on analysis 76.3 per cent of vanadium including a trace of iron. On dissolving in hydrochloric acid a little hydrogen came off.

Preparation "K."—34 grams of vanadium trioxide and 23 grams of potassium. There was a small hole in the top of the cylinder which was closed with a plug when potassium ceased

to burn at the hole. The cylinder was cooled under water. Yield 15 grams with vanadium content of 76.8 per cent. The water solution was reddish but lost color on standing, showing that a vanadite was present which slowly changed to vanadate. The reaction of potassium on vanadium trioxide evidently is



since, according to these equations the yield of 34 grams of vanadium trioxide is 15.1 grams of the dioxide and 15 was obtained. The first equation represents an endothermic reaction since the heat of oxidation of vanadium dioxide to trioxide is 145,000° and that of the oxidation of potassium is 97,000°, but the reaction of the system is exothermic and that of $\text{V}_2\text{O}_5 + \text{K}_2\text{O}$ is greater than 97,000°. A portion of "K" was placed in water in a tube through which a current of hydrogen was passing to displace the air, the water was boiled, then hydrochloric was added; the substance dissolved forming a green solution and *no* gas was evolved. I do not understand the reaction for V_2O_5 should yield VCl_3 , which should set free hydrogen with formation of VCl_4 .

In the following the calorimetric experiments preparation "H" was used in 11 and "K" in 12 and 13.

	11	12	13	
Vanadium dioxide	1.7374	2.002	2.104	grams
Sodium peroxide	6	8.3	8.6	"
Water equivalent of system	2898	3093	3067	"
Temperature interval	1.565°	1.589°	1.677°	
Heat effect	4535	4915	5143	
" " iron	-40	-40	-40	
" " oxygen evolved	+109	+220	+230	
	<hr/>	<hr/>	<hr/>	
	4604	5095	5333	
For 1 gram V_2O_5	2650°	2545°	2535°	

Two determinations made with preparation "J." which was not very pure, gave 2810 and 2799°. The results thus obtained with different preparations vary somewhat, but those of 12 and 13 are to be regarded as the best and give 340,000° for the heat effect of one gram molecule of vanadium dioxide reacting with sodium peroxide.

Experiment 14.—1.173 gram of "K" V_2O_5 was burned in oxygen as described in Exp. 9. Most of the product of the combustion was in one globule which externally had the color of the pentoxide but otherwise was black and crystalline. The atomic ratio of the vanadium to the oxygen in it was found to be 1 to 2.2. The heat effect observed less than of the cotton used was 1819°. Hence $1819 \div 1.173 \times 134 = 208,000^\circ$ for the heat effect of V_2O_5 burning chiefly to V_2O_4 .

Summary of Results.

$2V + 5O = V_2O_5 + \dots$	probably greater than	441,000° †
$V_2O_5 + 3Na_2O = 3Na_2O.V_2O_5 + \dots$		165,800 *
$V_2O_5 + 2Na_2O + Na_2O = 3Na_2O.V_2O_5 + \dots$		214,800 *
$2Na_2O + 2O = 2Na_2O_2 + \dots$		38,800
$V_2O_5 + 2O + 3Na_2O = 3Na_2O.V_2O_5 + \dots$		253,600
$V_2O_5 + 3Na_2O = 3Na_2O.V_2O_5 + \dots$		165,800
$V_2O_5 + 2O = V_2O_5 + \dots$		87,800 †
$V_2O_5 + Na_2O + 2Na_2O = 3Na_2O.V_2O_5 + \dots$		174,600 *
$Na_2O + O = Na_2O_2 + \dots$		19,400
$V_2O_5 + O + 3Na_2O = 3Na_2O.V_2O_5 + \dots$		194,000
$V_2O_5 + 3Na_2O = 3Na_2O.V_2O_5 + \dots$		165,800
$V_2O_5 + O = V_2O_5 + \dots$		28,200 †
$V_2O_5 + 3Na_2O = 3Na_2O.V_2O_5 + \dots$		340,000 *
$3Na_2O + 3O = 3Na_2O_2 + \dots$		58,200
$V_2O_5 + 3O + 3Na_2O.V_2O_5 + \dots$		398,200
$V_2O_5 + 3Na_2O = 3Na_2O.V_2O_5 + \dots$		165,800
$V_2O_5 + 3O = V_2O_5 + \dots$		232,400 †
$V_2O_5 + O = V_2O_5 + \dots$		140,600 †
$V_2O_5 + 2O = V_2O_5 + \dots$		204,200 †
$V_2O_5 + O = V_2O_5 + \dots$		59,600° †

* Experimental result.

† Derived result.

The heat effect of $V_2O_5 + O$ found by burning in oxygen in Exp. 9 was 55.2°, but the method was unsatisfactory, for in another experiment but little of the vanadium trioxide burned. Vanadium dioxide, however, burned well and gave in Exp. 14 for $V_2O_5 + 2O = V_2O_5 + 208,000^\circ$. This is a little high since some pentoxide was formed, but it confirms the result by the sodium dioxide method.

The striking fact observed in the results is the high heat of oxidation of vanadium dioxide, also that the results obtained with impure metal indicate that each of the first two atoms of oxygen combining with vanadium do not give a greater heat effect than the third atom. Assuming that they give the same, we have $2V + 5O = V_2O_5 + 520,000$ and only 441,000° were found.

After the foregoing paper was written the article on vana-

dium by Ruff and Martin* appeared. They find for the heat of formation of vanadium pentoxide 250,500°, a value much lower than the writer's results indicate. For example, $V_2O_5 + 2O = 204,000^\circ$ by the sodium dioxide method and confirmed, as already stated, by combustion in oxygen, points plainly to over 400,000° for the heat of formation of vanadium pentoxide, for it must be assumed that the first two atoms of oxygen give as much heat as the last two.

In view of Ruff and Martin's result it seemed desirable to burn vanadium in oxygen. The best material available was preparation "C," which contained 89.7 per cent of vanadium when first made, and 88.6 per cent four months later. It contained a trace of magnesium. The determinations were made as in Experiment 9, and the oxygen was at a pressure of 15 atmospheres. The product of a combustion formed a globule in the bottom of the bomb, small drops adhering to the top, and a dark red powder. The temperature of the combustion was high, and in one instance the heavy platinum electrode was fused. The following table indicates in part the details of the work :

	15	16	17
Metal taken (a).....	1.141	1.428	1.695 gram
Cotton ".....	0.075	0.069	0.071 "
Heat effect.....	3419°	4172°	4578°
" " of cotton.....	300	280	284
" " of a (b).....	3119°	3892°	4294°
Oxygen taken up by a (c).....	0.582	0.650	0.750 gram
Heat effect of 1 gram of oxygen $\frac{b}{c}$	5319°	5990°	5720°
Composition of product of combustion.....	V_2O_5	V_2O_5	V_2O_5

The average for 1 gram of oxygen combining with the oxidized metal is 5690°. For 4.2 gram atoms of oxygen is $5690 \times 16 \times 4.2 = 382,000^\circ$. This is the heat effect of the oxidation of a mixture of vanadium and vanadium oxide, containing a large proportion of the latter. Hence the result is much less than the pure metal should give. It is impossible to make allowance for the oxide, but on any assumption the correction will be large.

Uranium.

It is remarkable that there are no thermal data on uranium compounds since the metal and dioxide burn well in oxygen.

* Zeitschr. f. angew. Ch., xxv, 49.

The heat of formation of the dioxide has been regarded as high because of difficulty of reducing it. Professor B. B. Boltwood generously furnished an abundance of pure uranyl nitrate for the investigation.

Metallic uranium was prepared by a method of Moissan* modified in some details. In the bottom of a steel cylinder 30 grams of sodium were placed and on top of it 40 grams in small pieces of a mixture of the double salt, $\text{UCl}_2\cdot 2\text{NaCl}$, and approximately two equivalents of sodium chloride. The latter happened to be in excess when the double salt was made. The cylinder was closed with a loose screw cap and heated to redness for 15 minutes. Most of the excess of metallic sodium volatilized and escaped about the screw cap; the little remaining in the cylinder was removed by alcohol. The sodium chloride was dissolved in deaerated cold water and then the metal was washed with water, alcohol, and ether, and dried *in vacuo*, over sulphuric acid. The metal was in the form of a friable mass. It was pulverized and passed through a millimeter mesh. The coarser portion ignited when rubbed in a mortar. For analysis the metal was dissolved in aqua regia, and the hydroxide precipitated by ammonia.

0.3222 g. gave 0.3766 g. $\text{U}_2\text{O}_5 = 99.2\% \text{ U}$

0.9001 g. " 1.0144 g. $\text{UO}_2 = 99.4\% \text{ U}$

The metal contained a trace of sodium. The second analysis was made nine days after the first one, and the results show that the metal did not oxidize in the desiccator in which it was kept. Nor did it gain weight for a time in ordinary air. The brown coating of oxide was a protective coating. Another lot of metal, made as before, gave on analysis the following:

1.0378 g. metal; 1.543 g. $\text{UO}_2 = 98.07\% \text{ U}$

1.0336 g. " 1.1482 g. $\text{UO}_2 = 97.93\% \text{ U}$

The metal was found to contain 0.07 per cent of sodium. Both lots of uranium were free from chlorine and carbon, and both dissolved slowly in hydrochloric acid and left a small residue. This was an uranium compound soluble in aqua regia. The metal was completely soluble in nitric acid.

After completing the calorimetric work, a third lot of uranium was made and the metal obtained was in fused pieces and friable lumps. From the latter grains a half to one millimeter in diameter were separated. The analysis of these gave U, 99.7, Na, 0.09 per cent. These grains were found to burn incompletely in sodium dioxide in the bomb and to give low results. Hence no further heat tests were made with this sample of uranium.

* C. R. cxvii, 1088.

The first five experiments were made with the metal containing 99·4 per cent of uranium, and the last two with the 98 per cent lot. From the result it is found that 1 gram of oxygen combining to form U_3O_8 gives a heat effect of 6590°. What is the composition of oxide coating on the metal taken is not known, but it probably is a lower oxide and hence the heat effect of its formation may be a little higher. However this may be, the product of 6590 by the oxygen content of metal taken is added to the observed heat effect in the following experiments :

	1	2	3	4	5	6	7	
Metal taken...	1·7294	2·1944	2·1136	2·8266	4·7255	5·0633	4·4108	grm.
Composition of metal U (a)...	1·7190	2·1812	2·1009	2·8096	4·6971	4·9611	4·3226	"
O (b)...	0·0104	0·0132	0·0127	0·0170	0·0284	0·1012	0·0882	"
Cotton	0·0899	0·1005	0·1012	0·0928	0·0822	0·0830	0·0795	"
Water equivalent of system,	1352	1343	1466	1329	2979	2995	2867	"
Temperature interval	1·301°	2·119°	1·916°	2·704°	1·857°	1·836°	1·674°	
Heat effect	2168°	2846°	2809°	3594°	5532°	5549°	4803°	
Heat effect of cotton	- 363	- 404	- 405	- 374	- 329	- 335	- 321	
Heat effect of b	+ 68	+ 87	+ 84	+ 112	+ 187	+ 666	+ 581	
Heat effect of uranium (c) ..	1873	2529	2488	3332	5390	5830	5063	
Heat effect 1 gram of uranium $\frac{c}{a}$	1089°	1169°	1184°	1186°	1147°	1175°	1176°	
Composition of product of combustion	$U_3O_{7.07}$	$U_3O_{7.63}$	$U_3O_{8.04}$	$U_3O_{8.00}$	$U_3O_{7.70}$	$U_3O_{7.08}$	$U_3O_{7.04}$	

Excluding the results of 1 and 5, in which the oxidation was less complete than in the others, the mean is 1178°. For the heat of formation of U_3O_8 we have $1178^\circ \times 238.5 \times 3 = 842,900^\circ$ at constant volume and $845,200^\circ$ at constant pressure.

The metal having 98 per cent of uranium was not all in a powder adapted for combustion with sodium dioxide, hence the friable pieces were broken up and only the fine powder used. It was now found to contain 97·5 per cent of uranium. Allowance is made as before for the oxygen content of the metal in reducing the following observations :

	8	9	
Metal taken	6.014	7.060	grams
Composition of metal { U (a) ...	5.864	6.884	"
{ O (b) ...	0.150	0.176	"
Water equivalent of system ...	2914	2932	"
Temperature interval	2.502°	2.930°	
Heat effect	7291°	8591°	
“ “ of iron	— 40	— 40	
“ of oxygen evolved	+ 126	+ 206	
“ “ b.	+ 988	+ 1160	
“ “ uranium (c)	8365	9911	
“ “ 1 gram of uranium $\frac{c}{a}$..	1426°	1440°	

The average, 1433° times 233.5, equals 341,800° for the heat of one gram atom of uranium reacting with sodium peroxide.

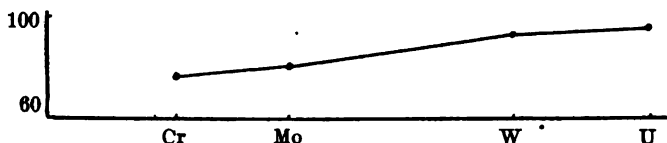
Heat of Combination of Uranic Oxide with Sodium Oxide.

Uranic oxide was made by heating cautiously uranyl nitrate in platinum until the mass solidified, then heating in a glass bulb to about 400° until the weight of the oxide remained constant. The preparation was found to be free from nitrate and to yield very nearly the theoretical amount of U_2O_5 . Another preparation of uranic oxide was used in experiments 12 and 13. The calorimetric work was as follows:

	10	11	12	13	
Uranic oxide	5.000	5.000	5.000	10.000	grams
Sulphur	1.000	1.000	1.000	1.000	"
Sodium peroxide ..	13.	13.	7.15	10.5	"
Water equivalent of system	3012	2786	3074	3056	"
Temperature interval	2.305°	2.351°	2.277°	2.685°	
Heat effect	6943°	7020°	6999°	8205°	
“ “ sulphur	— 5270	— 5270	— 5270	— 5270	
“ “ iron ...	— 40	— 40	— 40	— 40	
“ “ oxygen set free	0	0	0	400	
Heat effect uranic oxide	1633	1710	1689	3295	
Heat effect for 1 grm. organic oxide	327°	342°	338°	330°	

In mean, $334 \times 286.5 = 96,100^\circ$ for the heat effect of $Na_2O + UO_2$.

It has been shown* that the heat of the reaction, $\text{Na}_2\text{O} + \text{RO}_2$, increased regularly with the atomic weights where R is chromium, molybdenum, and tungsten. Uranium falls a little below the line extended from the others as shown in the figure in which the atomic weights are platted as abscissas and the heat effects as ordinates.



Uranium forms peruranates, hence the question, Do uranium oxides react in fusion with sodium peroxide to make a peruranate? The calorimetric results show that only sodium uranate results, since in experiment 12, where the amount of sodium dioxide present was only sufficient to form sodium sulphate, the heat effect is the same as it was in the other experiments with an excess of dioxide. All of the fusions in the bomb were orange color. Those of 10 and 11 mostly dissolved in cold water with evolution of oxygen, yielding an orange or reddish solution of peruranate. The solution, gradually at room temperature and quickly on boiling, became lighter colored and deposited a hydrous mixture of uranates having approximately the composition $3\text{Na}_2\text{O}, 8\text{UO}_3 + \text{XH}_2\text{O}$. The solution of peruranate mentioned was the result of the action of water on the mixture of sodium uranate and dioxide, for it was found that the former dissolves in a cold solution of sodium dioxide with formation of peruranate.

Uranium Dioxide.

Uranium dioxide was made by reducing the trioxide mixed with a little green oxide by hydrogen at a dull red heat. The combustions with sodium dioxide were as follows:

	14	15	16	
Uranium dioxide.....	5.000	10.000	5.000	grams
Sulphur.....	1.000	1.000	1.000	"
Sodium dioxide.....	14.	14.	14.	"
Water equivalent of system.....	2967	3101	3077	"
Temperature interval....	2.478°	3.037°	2.393°	
Heat effect.....	7352°	9418°	7363°	
" " of sulphur..	- 5270	- 5270	- 5270	
" " of iron	- 40	- 40	- 40	
" " of UO_3	2042	4108	2053	
" " 1 gram UO_3 ..	408°	411°	410°	

* This Journal, xxix, 490.

The average, $410^\circ \times 270.5 = 110,900^\circ$ for the heat effect of $\text{UO}_2 + \text{Na}_2\text{O}_2 = \text{Na}_2\text{UO}_4$.

In the following combustions of uranium dioxide with oxygen the same lot of dioxide was used except in the 21st experiment. For this the dioxide was from the reductions of the higher oxides resulting from burning the dioxide in oxygen.

	17	18	19	20	21
Uranium dioxide (a) ...	9.262	11.304	12.000	10.400	51.40 grms.
Cotton	0.1148	0.0957	0.1025	0.1048	0.304 "
Composition of product of combustion	$\text{U}_3\text{O}_{7.90}$	$\text{U}_3\text{O}_{7.98}$	$\text{U}_3\text{O}_{7.81}$	$\text{U}_3\text{O}_{7.92}$	$\text{U}_3\text{O}_{7.98}$
Uranium dioxide burned to U_3O_8 (b)	8.799	11.247	10.810	9.984	50.11 "
Water equivalent of system	1383	1384	1281	1292	2619 "
Temperature interval ..	0.905°	1.048°	1.132°	1.006°	2.139°
Heat effect	1251°	1450°	1450°	1300°	5664°
" " of cotton	-461	-386	-414	423	1211
" " of UO_2 (c) ...	790	1064	1036	877	4453
" " 1 gram $\text{UO}_2 \frac{c}{b}$	90°	95°	96°	88°	87°

The mean, $92^\circ \times 270.5 = 24,900^\circ$ at constant volume and $25,100^\circ$ at constant pressure for the heat of oxidation of 1 gram molecule of uranium dioxide when U_3O_8 is the product.

Urano-Uranic Oxide.

This oxide, U_3O_8 , used in experiments 22 and 23, was made by igniting the nitrate, then heating the residue and allowing it to cool slowly in oxygen. The weight was unchanged when heated and coated again in oxygen. The oxide used in experiment 24 was that formed by burning uranium dioxide in experiment 21, and which has the composition $\text{U}_3\text{O}_{8.00}$.

	22	23	24
Urano-uranic oxide	10.000	10.000	10.000 grams.
Sulphur	1.000	1.000	1.000 "
Sodium dioxide	13.	12.8	13. "
Water equivalent of system ..	3075	3047	2867 "
Temperature interval	2.737°	2.757°	2.949°
Heat effect	8416	8400	8454
" " of sulphur	-5270	-5270	-5270
" " of iron	-40	-40	-40
" " of oxygen set free	+281	+282	+313
" " of U_3O_8	3387	3372	3467
" " 1 gram of U_3O_8 ..	339°	337°	347°

The last result should not be included in the final value since the oxide used in the experiment contained a small excess of the dioxide. The average of experiments 22 and 23 is 338°. For 1 gram molecule of U_3O_8 , the result is 285,100°. Experiment 24 shows that the U_3O_8 formed at high temperature does not differ essentially from the ordinary so-called green oxide.

Summary of Results.

$3U + 4O = U_3O_8 +$	845,200° *
$U + 3Na_2O_2 = Na_2UO_4 + 2Na_2O +$	341,800 *
$3Na_2O + 3O = 3Na_2O_2 +$	58,200
$U + 3O_2 + Na_2O = Na_2UO_4 +$	400,000
$UO_2 + Na_2O = Na_2UO_4 +$	96,100 *
$U + 3O = UO_3 +$	303,900 †
$UO_2 + Na_2O_2 = Na_2UO_4 +$	110,900 *
$Na_2O + O = Na_2O_2 +$	19,400
$UO_2 + O + Na_2O = Na_2UO_4 +$	130,300
$UO_2 + Na_2O = Na_2UO_4 +$	96,100 *
$UO_2 + O = UO_3 +$	34,200 †
$3UO_2 + 2O = U_3O_8$ mean +	75,300 *
highest +	78,100 *
$U_3O_8 + Na_2O_2 + 2Na_2O = 3Na_2UO_4 +$	285,100 *
$Na_2O + O = Na_2O_2 +$	19,400
$U_3O_8 + O + 3Na_2O_2 = 3Na_2UO_4 +$	304,500
$3UO_2 + 3Na_2O = 3Na_2O UO_2 +$	288,300
$U_3O_8 + O = 3UO_3 +$	16,200 †

* Experimental result.

† Derived result.

From the foregoing data the following are derived from the combustions with

	Oxygen	Sodium dioxide
$3U + 4O_2$	845,200°	895,500°
$U + O_2$	256,600	269,700
$3UO_2 + O_2$	75,300	86,400

The results with sodium dioxide are 5 per cent higher than with oxygen in the first two cases and 11 per cent in the last. Regarding the accuracy of the various figures this may be said: 845,200 is to be regarded as good since it is the mean of closely results of burning in oxygen two different samples of metal with different contents of oxygen. If it be assumed that the oxide on the metal is UO_2 instead of U_3O_8 , which was taken as the basis for correction in experiments 1 to 7, the result will be a little higher. The burning of uranium dioxide in

oxygen gave results differing widely in percentage but only 9° per gram. If the highest be taken, then $3\text{UO}_3 + \text{O} = 77,900^\circ$, and this will make the derived figure for $\text{U} + \text{O} = 255,400^\circ$. Regarding the figures under sodium dioxide it will be observed that the results $895,500^\circ$ and $269,700^\circ$ are derived from combustions of the metal and that the correction for 2.5 per cent of oxygen is large, while 86,400 is derived from the combustion of UO_3 and U_2O_5 . It would appear that the results with sodium dioxide are not reliable. But it has been shown in previous papers that the method gives results with carbon, sulphur and titanium which agree closely with those obtained by burning in oxygen. In conclusion it may be stated that no explanation has been found for the high results by sodium dioxide.

ART. XVI.—*The Chattanooga Series with Special Reference to the Ohio Shale Problem*; by E. O. ULRICH,* Washington, D. C.

Introductory matter.—It is many years since I began to doubt the validity of the classification of the Devonian-Waverlyan shales in Ohio which was introduced in its essential features by Newberry in 1870, and with occasional modifications has prevailed to the present day. But it is only in the past two years that I have sufficiently investigated the mass of available evidence to permit me to take a decisive stand on the several intricate questions which are involved in the general problem.

Even in the past year, when I published correlation tables covering the formations in southeastern North America between the base of the Cambrian and the base of the Pennsylvanian in my Revision of the Paleozoic Systems,† I was not yet prepared to give a definite opinion respecting the relations of the greater part—commonly the lower half to three-fourths—of the typical Ohio and New Albany shales. On plate 28 (op. cit.) it is to be noted that the Chagrin formation is placed at the top of the Devonian. Beneath this, in the same column, as also in the two columns to the left, are found indefinitely limited spaces designated “lower part of Ohio shale” and “lower New Albany shale.” In both cases I referred to certain shales which are locally found at the base of the Ohio and New Albany shales and which contain fossils strongly suggestive of Genesee and Portage ages. On plate 29 the Waverlyan is begun with the Cleveland shale in Ohio,‡ the upper part of

* Published by permission of the Director of the U. S. Geological Survey, who, in view of the fact that this paper uses a new classification, at variance with adopted usage, disclaims responsibility for the classification, correlations, names, and re-definitions.

† Bull. Geol. Soc. of America, vol. xxii, pl. 27-29, 1911.

‡ A note of explanation seems desirable here. When these charts were drawn it was my intention to extend the limits of the Cleveland shale downward to the first diastrophic break. At Cleveland this meant to the base of the black shale to which the name was originally applied and which there is in contact with the Chagrin; 8 to 15 miles west of Cleveland it meant the same black shale plus 1-100 feet of softer shale (now called Olmsted shale) which is added without break to its bottom by underlap; and in Erie County it meant both of these shales plus the rest of the “Huron” down to the base of the *Dinichthys herzeri* beds, which in going westward are similarly added to the bottom without notable evidence of break. In other words, it was my purpose to apply the term Cleveland to the whole series of shales beginning with the concretionary *Dinichthys herzeri* beds and ending with the top of the black shale, which alone has hitherto been referred to under that name. This intention was based on the conviction that all of these beds are only parts of a single, though lithologically tripartite, formation which loses more and more of its members by overlap eastwardly from Erie County until the last finally disappears in northeastern Ohio. Chiefly for the reason that this tripartite formation is strictly equivalent to the Ohio shale of Andrews, my former purpose is now abandoned.

the New Albany shale in Indiana and western Kentucky, and with the Hardin sandstone member of the Chattanooga shale in Tennessee. But the Ohio shale, except its basal part, is not mentioned on either chart.

The innovations suggested in these charts, also certain statements respecting the Chattanooga shale in Tennessee and its relations to the Cleveland shale of Ohio published by Dr. R. S. Bassler a few months earlier in the same year,* led Dr. E. M. Kindle to express his dissatisfaction over the delay in publishing my evidence. The present paper is intended primarily to supply this deficiency in so far as it may be done in the space here allotted to me. Obviously, however, considering the magnitude and intricacy of the task, and the abundant literature bearing more or less directly, though often diversely, on one or another of its many subsidiary problems, the present effort is necessarily far from exhaustive or even from being satisfactory to myself. Still, if because of lack of space and time I fail to establish the fundamental features of my contention, I yet believe that I shall succeed at least in transferring the burden of proof to those who have assumed that the Chagrin formation belongs between the Huron shale beneath and the Cleveland shale above, and who, on the basis of the universally admitted late Devonian age of the Chagrin and its assumed superior position, have correlated the "Huron" with other Devonian formations. Now that these assumptions are questioned, they must prove by unequivocal stratigraphic and faunal evidence that the Chagrin formation actually overrides the *Dinichthys herzeri* zone. Or, if that can not be done with absolute certainty, they must at least prove that the Huron fish fauna is actually a Devonian facies and not, as I believe it, a derivative of Devonian fishes that persisted with slight modification across the systemic boundary into the initial stage of the succeeding Waverlyan system. Finally, they must offer a satisfactory explanation of the anomaly indicated by comparisons between the Huron and Cleveland faunas on the one hand and the Chagrin on the other. They must show particularly why the fishes and conodonts in the Huron and Cleveland shales are so closely and undeniably similar in kind whereas the same classes of fossils, especially the fish remains, in the supposed intervening Chagrin shale and in its late Devonian equivalents in Pennsylvania and New York, differ so markedly.

Chief points to be discussed in present paper.—From the foregoing statements and the correlation charts recently published it is evident that I differ radically on three points from the views now commonly held respecting the strati-

* Bassler, R. S.: The Waverlyan Period in Tennessee, Proc. U. S. Nat. Museum, vol. xli, pp. 209-224, 1911.

graphic sequence and correlation of the Devono-Waverleyan black shale series in Ohio, Indiana, Kentucky, and Tennessee. The first departure concerns the stratigraphic position of the Chagrin formation (Erie shale of Newberry) with respect to the Huron shale of the Ohio geologists. Beginning with Newberry in 1870 and continuing to the present day, all geologists who have worked on this part of the Ohio section have placed the Chagrin *above* the Huron. I insist that this relation of the two formations has never been established, and that most probably the opposite condition obtains; in other words, that the Huron is younger, and not older, than the Chagrin. Incidentally it will appear that the beds beginning with the concretionary *Dinichthys herzeri* zone (which usually forms the lower part of the Huron) and ending with the top of the Cleveland shale, constitute a single broadly conceived and diastrophically unbroken formation, or a group of three lithologically distinguishable members, which overlaps eastwardly over the edge of the westwardly diminishing wedge of Chagrin shale. It will appear, further, that these oppositely directed overlaps are explained on the ground of continental tilting by virtue of which the marine waters in which the Chagrin and other late Devonian deposits in eastern Ohio and contiguous areas were laid down, invaded from the north middle Atlantic, while those making up the Huron-Cleveland, or Ohio shale, group invaded from the Gulf of Mexico.

The second difference concerns the equivalents in the northern Ohio section of the Chattanooga shale of Tennessee and Kentucky. Formerly the "Black shale" in these southern states was rather generally regarded as corresponding approximately to the Genesee shale of New York. Later it was learned that, in the Ohio valley at least, this shale comprises a continuation of the Cleveland shale, and as the latter was known to overlie beds with a Chemung fauna, it at the same time became obvious that, while the basal part of the Ohio shale, as it was then commonly named, might be of Genesee age, its top could not be older than late Chemung. Finally, after Foerste and Morse* had shown that the black shale of south central Kentucky is not limited above by the top of the Cleveland, but that its upper part includes an hiatus which opens northwardly from the vicinity of Irvine to make room for a wedge of Bedford shale and Berea sandstone that finally expands to a thickness of 118 feet at the Ohio, the way had been paved for a revised conception of what the Chattanooga shale might really

* Jour. Geology, vol. xvii, pp. 164-167, 1909.

be.* It had, in fact, been established that the Chattanooga shale of the London and Richmond folios of the U. S. Geological Survey Atlas comprised not only the Ohio shale of Andrews but also the southern extension of the Sunbury shale of Ohio. Moreover, the work of Foerste and Morse made it highly probable that the Chattanooga, as developed in different parts of Tennessee, may occasionally consist of representatives of only the Cleveland, and in other cases of only the Sunbury shale of the Ohio section. Finally, it had become reasonably probable, not to say positively assured, that the outcrops of typical Chattanooga shale in east and middle Tennessee never included beds older than the Cleveland.

The third point on which my views differ strongly from those now commonly held pertains to the taxonomy of the beds involved in this discussion. Beginning with the publication of Newberry's classification in 1870-73, the base of the Waverlyan has been drawn by many geologists at the base of the Cleveland. In 1886-8, however, Orton repeatedly expressed his disapproval of Newberry's arrangement and transferred the Devono-Waverlyan boundary to the base of the Bedford shale, a step in which he was followed by the majority of American geologists. The removal of the Cleveland to the Devonian was occasioned by his inability to discriminate successfully between the three formations—the Huron, the Chagrin (Erie), and the Cleveland—which in the order named were thought to fill the interval between the Delaware limestone

* Much to my surprise, I learn that there are yet a few geologists who do not admit a stratigraphic hiatus within the Chattanooga shale at Irvine. Do they bear in mind all the facts in the case when they explain the pinching-out of the Berea and Bedford as mere thinning of deposits without interruption of sedimentation by emergence? Apparently no one doubts that the bed of black shale overlying the thinned extremity of the Berea-Bedford wedge at Irvine is Sunbury and that the black shale beneath the wedge is, if not exactly Cleveland, at least pre-Berea in age. And those acquainted with the subject know that the Berea-Bedford wedge expands from practically nothing at Irvine to between 200 and 300 feet locally in northern Ohio. What was going on in southern Kentucky when these thick deposits were being laid down in northern Ohio? But more than that, do these sceptics remember that the Berea in northern Ohio, even where best developed, is separated by a clearly defined unconformity—hence an hiatus—from the Bedford shale which underlies it? Most probably also there is an hiatus between the Cleveland and the Bedford, and perhaps another between the Berea and the Sunbury. Now what becomes of these in part definitely established hiatuses when the formations bounded by them pinch out entirely so as to bring the Sunbury in contact with the Cleveland? As I see it, merely this—they are merged in a greater hiatus. To deny this is to fly in the face of absolute fact and logic. That the increased hiatus is inconspicuously indicated is not extraordinary. Stratigraphic breaks between shale formations, even when the time is long, are always inconspicuous. But however obscure to the uninstructed, the evidence of a stratigraphic hiatus even in these cases is indubitable and obvious enough to those who have mastered the criteria sufficiently to recognize the break when it is before them.

(or the Olentangy shale when present) and the Bedford shale. Under the accepted belief that the Chagrin overlies the Huron, Orton's proposal was fully warranted on the grounds of logic and convenience in classification. But if it can be shown that the Chagrin, in which I see nothing else than the westwardly overlapping continuation of the Chemung of Pennsylvania and New York, is really older than the Huron, then the most convincing of the reasons on which he based his contention that the Cleveland should be placed in the same system to which the Chemung and Chagrin are referred, are materially weakened if not entirely set aside. In that case too, the striking similarities exhibited by the faunas of the Cleveland and Huron no longer call for explanation, while the no less notable faunal discordance between the Chagrin and the Huron also is readily understood.

The most widely recognizable and on all counts the most important of the breaks that have been determined in the Devonian and Waverlyan deposits of southeastern North America, is the one marking the overlapping base of the so-called Devonian black shale. This boundary is everywhere sharply defined. It is always unconformable; and the time value of the stratigraphic hiatus which it marks varies greatly from place to place. At one point the black shale is in contact with an Ordovician formation, at another with Silurian, at still other places with early, middle, or late Devonian formations. And very decided crustal movements preceded and progressively induced the advance of the waters in which these black shales were laid down. Thus, during the late Devonian (Chemung) the middle Appalachian region was submerged and invaded by Atlantic waters which finally extended over the eastern third or half of Ohio. During the Chattanooga, on the contrary, the surface of the continent tilted so that these Chemung areas were emerged and the southern areas, which for a long time prior to this had formed part of a great median land mass, sank beneath waters invading from the Gulf of Mexico. This submergence left a great thickness of siliceous shale (Woodford) in Oklahoma. In Ohio it left the three divisions of the Ohio shale, the Huron, Olmsted, and Cleveland, all of which—the second and third certainly and the first probably—thin by overlap eastwardly across northern Ohio until the last is finally lost before reaching the Pennsylvania border. All of these facts and criteria positively indicate that extraordinary geographic changes set in following the close of Chemung sedimentation in Ohio. Decided faunal changes too were introduced. What more evidence need be offered in testing the propriety of drawing the Devono-Waverlyan boundary at the top of the Chagrin in Ohio and not at the top of the Cleveland?

Desirability of method in drawing stratigraphic boundaries.—The location of systemic boundaries in stratigraphy, indeed of all formational boundaries that are not based purely on lithologic changes, is a matter of method. But the same method should be used in all cases. If this is granted, namely, if consistency is admitted to be an essential feature of method, and if the basic principle of our method is the introduction of new faunal elements, of new seas and of other new physical conditions, then I would say that we can not avoid closing the Devonian at the hiatus marking the top of the Chagrin; for if the Helderbergian is Devonian and the Morrow group of Arkansas Pennsylvanian, both of which represent the first invasions of the sea following a long state of emergence, then for the same reasons the whole of the Chattanooga is Waverlyan. That the general aspect of the faunas in these introductory deposits often retains much that recalls faunas of the next preceding period is to be expected. This is more especially true of faunas which invaded from the same oceanic basin. Organisms modified slowly in these and in no case known to me was the change from one period to the next complete. There are always some forms which survived for a time into the succeeding stage.

In further explanation of my attitude respecting the age of the Chattanooga it should be added that until it is actually proved that the Chagrin belongs between the Cleveland and the Huron and not, as I believe, beneath both, I must insist that the Waverlyan begins in Ohio with the *Dinichthys herzeri* zone of the Huron. True Devonian black shales—even younger than the Olentangy, which also at times was included in the Huron—may occur locally beneath the Dinichthys zone, but these are not to be considered at this time.

The Term Chattanooga.—As regards the standing and significance of the term Chattanooga, its wide and varied use by the geologists of the Federal Survey makes it clear that it was intended to cover all the black shale zones between the middle Devonian and the first limy or sandy beds of the Mississippian. This evident intention gives the term a somewhat broader significance than is warranted in practical taxonomy. There are two sets of black shales in this wide interval, a lower of which the Genesee is the chief element and an upper of which the more important members are comprised in the Ohio shale. Now as it is the later of the two that is represented at Chattanooga it seems to me proper to confine the name derived from this locality to this upper series. As developed at Chattanooga and in middle Tennessee, the Chattanooga includes only the upper member or members of the series. In central Kentucky however, where Campbell* mapped the black shale series

* Campbell, M. R.: Folios Nos. 46, 47, U. S. Geol. Survey Atlas, 1898.

as Chattanooga, we have the fuller representation that has induced me to use this term for the whole series. Here the Chattanooga shale begins with a representative of the Huron and includes at its top the Sunbury shale, which, through the pinching out of the normally intervening Bedford and Berea, has come in contact with the Cleveland. That this relatively complete representation of at least the black shales of the series—possibly the Bedford and Berea are everywhere absent to the south of Irvine, Kentucky—occurs beneath the load of younger rocks in the Cumberland plateau, also that only its upper beds have extended far enough by overlap to outcrop in the vicinity of Chattanooga, seems too probable to require proof. If I were to mention any of the evidence on which the latter probability is based it would be a dilation on the fact that fossil shells collected in the typical Chattanooga when compared with specimens of *Lingula melie* and *Orbiculoidea herzeri* from the Sunbury at Berea, Ohio, proved absolutely indistinguishable to several observers.

Chattanooga series a hitherto unrecognized division of the time scale.—The chief result of these studies is not so much a matter of correlation whereby certain formations are removed from one system to another as that a distinct and almost wholly new division of the time scale, of the rank of a series, is intercalated between the top of the Devonian and the base of the Kinderhookian with which the Mississippian system of prevailing classifications begins. The top of the Devonian remains as before, being drawn at the close of the Chemung. If the Catskill contains younger beds than the Chemung it is believed that they are chiefly intersystemic land deposits whose age is in part if not wholly pre-Chattanooga; and if any of them are really younger than the beginning of the Chattanooga then it is likely that they will finally be shown to correspond to such of the Waverlyan formations as the Bedford, the Berea, and certain still younger deposits that now fall within the rather broad interval covered by the Cuyahoga formation. Only very detailed stratigraphic studies can settle these questions. However they may turn out they can not materially affect a classification based primarily on marine deposits. The fact then remains that the Chattanooga is an essentially new series that had not heretofore been recognized in our geological time scales. It is new in that it comprises six formations of which the oldest is placed above the Chemung and the youngest beneath the Louisiana limestone. The last, as is well known, is the oldest of the formations in the Mississippi Valley now referred to the Kinderhookian. Hitherto the Chattanooga formations were divided between the Devonian and the Mississippian, the lower three being indefi-

nately correlated with Neodevonian formations in New York while the upper three were correlated in a similarly generalized manner with the Kinderhookian. That the last of the Chattanooga deposits is older than the Louisiana limestone is inferred primarily from the fact that the Sunbury is recognized in the upper part of the Chattanooga shale of central Tennessee; and secondarily from the belief that the thin bed of black

General time scale			OHIO			KENTUCKY	TENNESSEE
Ulrich 1912			Ulrich 1912	Newberry 1870-8	Orton, Prosser, and geologists generally since 1898	Ulrich 1912	Ulrich 1912
WAVERYLYAN	Chattanooga	Osganian	Logan ss. Black Hand conf. Cuyahoga f. (Break)	Waverly group	Logan ss. Black Hand conf. Cuyahoga f.		Chattanooga shale
		Kinderhookian					
		Sunbury	Sunbury sh.		Sunbury sh.	Sunbury	Sunbury
		Berea	Berea ss.		Berea ss.		?
		Bedford	Bedford sh.		Bedford sh.		
		Cleveland	Cleveland sh.		Cleveland sh.		Cleveland
		Olmsted	Olmsted sh.				
		Huron	Huron sh.	Erie sh. (1870)			(Absent)
DEVONIAN	Neodevonian	Chemung	Chagrin f. (? Break)	Erie sh. (1870-3)	Cleveland Ohio shale Chagrin (Erie)	Absent	
		Portage		Huron	Huron	(? Genesee)	
		Genesee	? Genesee sh.				

Table showing varying views concerning the taxonomic relations of the Devonian and Waverlyan black shales of Ohio, Kentucky, Tennessee, and New York.

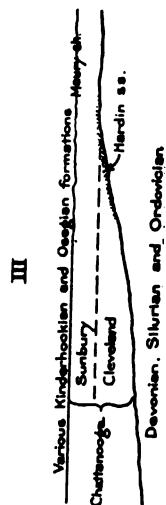
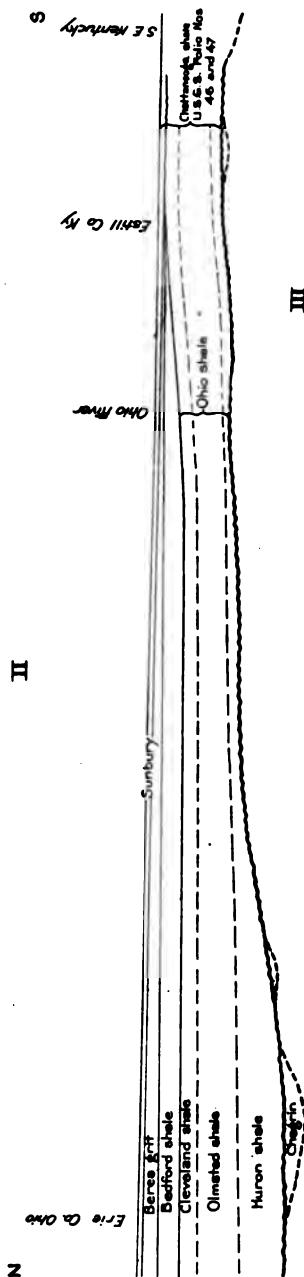
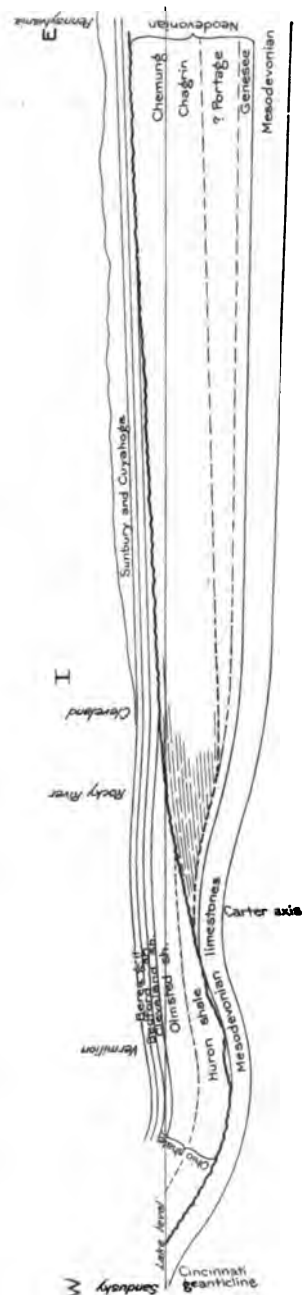
shale which underlies the Louisiana in Lincoln County, Missouri, represents the final, rather than any older, stage of the Chattanooga transgression in the Mississippi Valley. The merits of the Waverlyan as a distinct system cannot be discussed here. Pending the full discussion that I hope to give at some future time, the reasons presented more or less incidentally in various parts of my Revision of Paleozoic Systems must suffice for the present.

In order that the intercalations and proposed changes in the classification and correlation of the various black shale formations involved in this discussion may be clearly understood, the accompanying table is presented. As will be observed, only the Chattanooga part of the scale is fully developed, the Neodevonian, Kinderhookian, and Osagian parts being more or less condensed.

The Chattanooga sequence in Ohio.

General statement.—No one as yet is sufficiently informed concerning the surficial and underground behavior of the Chattanooga formations in Ohio to write them up in a comprehensive and thoroughly reliable manner. Yet so much has been published about the great shale series in the Ohio state reports that detailed descriptions seem unnecessary here. Only a very generalized account will be attempted. Here and there we may have to enter into some details which are thought to have a more than usually direct bearing on the problems at issue.

Huron shale.—Beginning at the north, the basal part of the series is formed by the Huron shale. This consists of 200 or 300 feet of mostly black shale which is distinguished from other shales of the series by the large calcareous concretions which it contains, especially in its lower half. These concretions are often a very conspicuous feature and in many cases they are formed about a fish bone or some other organic nucleus. The formation outcrops in a belt of varying width that extends entirely across the state from the lake shore in Erie County to and across the Ohio into Kentucky. The Huron evidently overlapped westwardly on the flanks of the Cincinnati axis so that in places only its upper beds are present. It seems also to have suffered diminution by overlap in an eastward direction, but how far from the line of outcrop such overlap thinning begins cannot be decided with the evidence in hand. Nevertheless we have indirect evidence in deep wells and surface relations suggesting that the Huron did not extend far beyond the Carter axis, an old line of uplift that passes through Carter County, Kentucky, and is indicated at intervals



EXPLANATION OF FIGS. I-III, p. 166.

FIG. I. Generalized schematic section due east and west from Sandusky, Ohio, to Pennsylvania state line, showing new conception of the stratigraphic relations of the Chagrin shales to the Huron, Olmsted, and Cleveland divisions of the Ohio shale. Vertical scale greatly exaggerated.

FIG. II. Similarly generalized section southward from Lake Erie to southeastern Kentucky, showing pinching out of the Bedford and Berea formations in central Kentucky, the inclusion of the Sunbury with the members of the Ohio shale in the Chattanooga and the southward thinning of the Huron in northern Ohio.

FIG. III. Section showing supposed overlap thinning of Chattanooga shale in Tennessee whereby the formation may be locally represented only by the Sunbury division.

southward through this state into Tennessee and northward through Ohio to the lake shore west of Cleveland.* The lower beds of the formation at least are thought to be confined to the shallow structural trough between the Carter and Cincinnati axes. At any rate, so far as I can learn, none of the deep wells to the east of the Carter axis have ever been reported passing through the hard calcareous concretions which are characteristic and widely distributed. So far as known, the Huron is always separated from underlying formations by a stratigraphic hiatus. At the top, however, no evidence of break has been observed.

Olmsted shale.—This name is proposed in a letter to me by Professor H. P. Cushing for the body of relatively soft, mainly blackish, though partly bluish shale which wedges in at the base of the Cleveland shale in West Cleveland, where it—first the typical Cleveland and then the intercalated bed—rests on and is sharply distinguished from the Chagrin formation. West from Cleveland the Olmsted shale gains with moderate rapidity, attaining a thickness of nearly 100 feet at the western edge of the Berea quadrangle. Though not traced beyond this point, I am confident that this shale expands still more to the west and finally passes into the middle member of the Ohio shale as developed in Erie and Huron counties. I believe further, and I may say that Professor Cushing is of the same opinion, that this Olmsted member constitutes the bulk of the Ohio shale seen in central and southern Ohio and of its exten-

*The northern extension of this axis is incorrectly represented in the small map on page 293 of my paper in Bull. Geol. Soc. America, vol. xxii, 1911. As drawn there two distinct axes are wrongly connected at the Ohio. The Carter axis passes farther west in Ohio and should run more nearly parallel to the Cincinnati axis.

sion in Kentucky,* in all of which places the Ohio shale is thinner than in Huron County and the Huron member especially inferior in volume.

Along Huron River the presumed Olmsted seems not to be sharply delimited from either the underlying Huron or from the overlying Cleveland shale. Neither boundary has been consistently drawn by geologists who have studied the rock in this area. Newberry, in his report on Erie County,† speaks of the top of the Huron as being interstratified with the lower beds of the "Erie" which he thought he recognized in the section of that county. Evidently the supposed Erie is what Cushing is calling the Olmsted. That he had trouble also in recognizing the boundary between the Cleveland and the Olmsted is evident enough from the fact that the fish beds near Avon Point, which according to Cushing and my own views certainly belong in the Olmsted, were first referred to the Huron on the erroneous assumption of continuous easterly dip, and later to the Cleveland.‡ In fact neither Newberry nor Orton recognized a formation boundary between the Cleveland and the Olmsted, and so far as I know there is no break between them. Nevertheless the two zones are widely distinguishable and should be recognized in refined stratigraphic work.

Cleveland shale.—The chief features by which the Cleveland shale is distinguished from the Olmsted are its relative hardness and slaty structure. Irregular concretionary masses occur in places, but they are less calcareous and seldom or never of the spherical form that characterizes the concretions in the Huron. The typical Cleveland, though varying in thickness and probably not exceeding 50 or at the most 60 feet, seems to

*In his paper on the Chattanooga shale in the February number of this Journal, Dr. E. M. Kindle refers to similar statements of authors, mentioning Professor Edward Orton, Jr. as "one of the first to claim that the black shale in central Kentucky is the upper or Cleveland Division." Concerning this it may be pointed out that the son was preceded by the father in this opinion, Prof. Edward Orton Sr. having published in 1888 (Ohio Geol. Survey, vol. vi, p. 26) an even more definite statement to the same effect. Further, the senior Orton, who was certainly not "unfamiliar with the subject," leaves the impression that his opinion was based not only on physical criteria but also faunal evidence, when, in his closing remark, he says "the shale that covers the Lower Silurian limestone in central Kentucky is the upper or Cleveland division, if the fossils can be relied on to settle the question." To make Orton's position on this matter clear with respect to Professor Cushing's and my own it should be said that he evidently regarded the Cleveland as a formation overlapping from the south and in consequence simply added these underlying Olmsted beds—in which he could recognize neither the Chagrin nor the typical Huron—to the base of the Cleveland. That I intended to follow him in this is evident from the note on page 157.

† Ohio Geol. Survey, vol. ii, p. 188, 1874.

‡ Newberry, J. S., Mon. U. S. Geol. Survey, xvi, p. 129, 1889.

be more widely and more evenly distributed than either of the underlying members of the Ohio shale. As already said, it extends as a practically continuous sheet at the top of the Ohio shale division of the Chattanooga from Lake Erie to Alabama. Here and there across this wide area it may be absent, in some cases evidently because it had pinched out by overlap on some old uplift. In other places, however, it may have been thinned and occasionally cut through by erosional processes prior to or during the areally more limited deposition of the succeeding Bedford and Berea.

Bedford shale.—This formation consists largely of light-blue or gray shales in part often reddened, especially near the base though also toward the top, with peroxide of iron. Commonly fine-grained sandstones, usually in thin layers, and often beautifully ripple-marked, are interbedded with the shales, but occasionally similar arenaceous matter forms irregular masses. The Bedford outcrops apparently in a continuous band across the state of Ohio, ranging in thickness between 50 and 100 feet. South of the Ohio it gradually pinches out along the line of outcrop, being unknown beyond Irvine, Kentucky. In an easterly and southeasterly direction from north central Ohio the formation probably extends underground into the neighboring states of Pennsylvania and West Virginia. In the logs of deep wells it is usually included with the underlying Ohio shales.

Berea grit.—In that it is intercalated between two bodies of shale, and hence easily recognizable, this extraordinarily persistent sandstone constitutes an extremely valuable datum plane in Ohio geology. In Lorain County the Berea is thicker than usual, locally attaining 225 feet. Elsewhere it seldom exceeds 50 feet. Unusual thicknesses have occasionally been reported also in deep wells to the southeast of Lorain County, even as high as 170 feet. In the latter cases it is thought likely that a considerable part of the excess should have been referred to the Bedford rather than the Berea. Commonly the rock is a fine-grained sandstone, usually in thin even layers, frequently ripple-marked, and occasionally with pebbles. Clay is usually present, mostly forming thin seams of shale, but it is never a very important constituent. In Lorain and Cuyahoga counties the sandstone is often of coarser grain and much of it relatively massive. The base evidently marks an unconformity that is locally conspicuous. The top also is very sharply distinguished from the overlying Sunbury shale. Regarding areal distribution, that of the Berea sandstone seems to be very nearly the same as the Bedford. It extends eastwardly into Pennsylvania and southwardly to Estill

County in central Kentucky, where both formations are finally lost.

Sunbury shale.—The Sunbury may be quickly described as a rather thin but extremely persistent bed of black fissile carbonaceous shale, usually much like the typical Cleveland in general aspect. In Ohio it ranges in thickness from 6 to nearly 28 feet. In Kentucky it is likewise very persistent though considerably thinner, being in places reduced to less than a foot. Since it is clear that the Sunbury followed differential tilting and warping of the continental basins that prohibited deposition of the Bedford and Berea in the same general area, it is inferred that this youngest bed of the Chattanooga black shales is gently overlapping in structure and that these greatly reduced thicknesses on the east flanks of the Cincinnati dome are ascribable to this cause. However, I have seen small accumulations of ill-stratified soft clay with phosphatic pebbles or nodules at the top of this Sunbury in Kentucky, a condition that suggests a time break following this shale and probably removal of some of its original thickness by erosion. In Tennessee, more particularly in the west middle part of the state, a similar break is indicated by the Maury shale, a thin glauconite bed often filled with phosphatized concretions, that probably represents surficial decomposition and subsequent recementation. This layer was referred to the top of the Chattanooga by Hayes and Ulrich,* which is correct if we consider chiefly the origin of its material. But if the date of its recementation and the fact that its top includes both reworked and transported material is brought into the foreground, the layer becomes debatable ground. On the latter grounds, I take it, Safford,† and more recently Bassler,‡ have classified the Maury shale as post-Chattanooga. There is, however, a practical objection to Safford's classification of the bed, namely, that in the distance of a mile or two the Maury would have to be placed at the base of two and rarely, even three, distinct formations, which successively overlap the margins of the narrow embayments that indented the shores of the Nashville island. Thus, in one case, the Maury would be at the base of the Ridgetop shale, an early Kinderhookian formation; in another, but a short distance away, the New Providence—early Osagian in age—is the first to rest on it, while in many other nearby places the recementation was delayed to the advance of the Fort Payne sea. For this reason

* Folio No. 95, U. S. Geol. Survey Atlas, 1903.

† Safford, J. M.: *Elements of Geology of Tennessee*, 1900, pp. 104, 141.

‡ Bassler, R. S.: *Proc. U. S. Nat. Museum*, vol. xli, pp. 209-224, 1911.

I leave the Maury in the position assigned to it by Hayes and Ulrich.*

As intimated at the head of the preceding paragraph the Sunbury shale is widely distributed. From Berea in northern Ohio it extends eastwardly to some unknown point—possibly beyond the Pennsylvania line—in which case it would seem to form the basal part of the Orangeville shale. Southwardly it has been traced by several observers, notably Prosser, across the state to Vanceburg, Kentucky, and thence by Foerste and Morse to the Kentucky River at Irvine. South of this point the Sunbury shale, through failure of the Bedford and Berea formations which underlie it in Ohio, rests with obscure but unquestionable unconformableness on the Cleveland. In Tennessee, finally, it is believed that in certain places the Sunbury alone represents the Chattanooga. In such places the Chattanooga shale, though very persistent, is usually less than 10 feet thick, as in the Columbia quadrangle. Both features are regarded as indicating gradual overlap across a nearly plane surface rather than diminution due to erosion subsequent to more complete deposition.

The Chagrin formation.

The Chagrin formation, or, as Newberry and the geologists of his Survey called it, the Erie shale, is not included in the Chattanooga series. In my opinion it is clearly late Devonian in age and older than the Huron member of the Ohio shale. Furthermore, on the basis of stratigraphic continuity and fossil contents, I can not see how we can avoid correlating the upper part at least of the Chagrin as Chemung, hence, according to the now prevailing interpretation of the New York standard, as latest Devonian. This correlation of the Chagrin was indubitably fastened by Newberry in the early seventies, and no one has since succeeded in materially shaking the conviction of those who accepted his view. It is therefore deemed

* It seems desirable here to correct a misapprehension that seems to have arisen in certain quarters respecting the reputed "migration" of the unconformity indicated at the top of the Chattanooga by Hayes and Ulrich in the Columbia folio. In the February number of this Journal, Mr. E. M. Kindle refers to this unconformity as "belonging to the evanescent class of unconformities." This unconformity is neither evanescent nor has it migrated to any other position than that assigned to it by Hayes and Ulrich. If Mr. Kindle had carefully read the text of the Columbia folio, he must have noted that this unconformity was not regarded by the authors of the folio as of high importance. For instance, at the close of the description of the Chattanooga, he would have found this statement: "Rarely as in the upper part of East Fork of South Harpeth Creek, the green, glauconitic shale usually at the top of the formation is absent or not distinguishable, and in these cases the black shale seems to pass very gradually into overlying calcareous green shale (now known as the Ridgetop shale) which is without glauconite and constitutes the base of the full Tullahoma section."

quite unnecessary to burden these pages with even a digest of the already frequently published evidence. The only point that might be brought out with profit here is that with the removal of the Chagrin wedge from between the Huron and the Cleveland to a position distinctly beneath the Huron, the paleontological evidence afforded by the upper part of the Chagrin is cleared of the suspicion that it may be a Portage facies of the Chemung fauna and not the Chemung proper. It is to be understood, however, that I have no intention of denying that the Chagrin, providing this formation is interpreted as including all the Neodevonian rocks found outcropping in northeastern Ohio, does not include beds of Portage as well as Chemung age. In fact I believe it does, though I question very much that the Portage, even as a thin wedge, extends as far westward in Ohio as the Chemung. The Genesee, too, I am willing to believe that it once extended as a thin deposit entirely across northern Ohio into the northern Indiana-Michigan basin. This sheet, together with portions of the Olentangy beneath it, which we know to be absent in many sections, would in that case have been rather generally removed by erosion prior to the Huron transgression. However, that is a phase of the general subject that may be readily set aside as having no vital bearing on the problems immediately before us.

Physical evidence bearing on the relative positions of the Chagrin and Huron formations.

General discussion.—It has long been known that the Chagrin thins rapidly in a westerly direction across northern Ohio from the Pennsylvania state line. Newberry originally believed that this formation pinched out also southwardly and that it was confined to the counties near or bordering Lake Erie. This is evident from a statement in his report on Erie county* where he says "it (the Erie shale) probably reaches but a little way back from the lake shore." It was this belief doubtless that led him to assign all of the Ohio shale in central and southern Ohio to the Huron. Further, it was generally accepted then that the rocks of northern Ohio dipped gradually and continuously eastward from Sandusky, a conception that was slightly modified when Newberry† discovered that beginning near the mouth of Rocky River the dip changes from east to west and that it continues westerly to Vermilion River. Finally, as concerns northern Ohio, it was not appreciated that whereas the Chagrin thins westwardly, the

* Ohio Geol. Survey, vol. ii, p. 188, 1874.

† Mon. U. S. Geol. Survey, xvi, p. 127, 1889.

Olmsted and Cleveland certainly, and most probably also the Huron, thin eastwardly and disappear entirely from the section before reaching the Pennsylvania line.

The great number of deep wells that have been drilled since Newberry's day in every part of Ohio in search of oil and gas have thrown a vast amount of light on the underground geology of the state. This new and otherwise unattainable information has already enabled us to correct many misapprehensions; and its use is by no means yet exhausted. It was the well records that induced Orton to abandon Newberry's view respecting the Huron in central Ohio, and to claim that the black shale series here "comprises all of the elements of the northern section. In other words, the so-called Huron shale of central Ohio is the Cleveland, Erie, Huron shale of northern Ohio."

Orton's quoted view helped matters considerably; and it is the accepted view today. But is it quite true? I believe not. As stated in the remarks on the Olmsted, I can not admit that any of the beds in the Ohio shale outcrops in central and southern Ohio are continuous with or of the age of the typical Chagrin in northeastern Ohio. On the contrary, the supposed representative of the Chagrin in the Ohio shale is the expanded southerly extension of the Olmsted, which, together with the underlying Huron and the overlying Cleveland shales, constitute a single formation or group that is but indefinitely divisible into the three lithologic members. The distinction of these members seems to grow more and more indefinite in a southerly direction from the lake shore, and to the south of the Ohio it is perhaps impossible to draw the lines between them with any degree of certainty. Even along Lake Erie I question if the top and bottom of the Olmsted can be everywhere sharply delineated.

Notes of thinning of shale complex as shown in deep wells.—As has been mentioned, the chief datum plane of the drillers in eastern Ohio is the Berea grit. The interval between the Berea grit and the underlying Devonian limestone is usually referred to as the Bedford and Ohio shales and reported as a unit. Now and then the Bedford is distinguished, especially when the red in its coloring matter is conspicuously developed. For the purposes of this discussion it will suffice to follow the drillers in lumping the shale mass beneath the Berea into a single undifferentiated complex. The term *shale complex* should therefore be understood as referring to this mass.

The complex as developed in a band some 30 or 40 miles wide, crossing the state in a north-south direction and bounded

* Ohio Geol. Survey, vol. vi, p. 25, 1888.

on the west by the outcrop of the Berea, doubtless comprises an average thickness of Cleveland shale. This formation probably extends farther under cover, but, judging from the fact that it pinches out eastwardly from Cleveland before reaching Trumbull County, it is thought unlikely that it is present under any of the eastern range of counties. The Bedford, however, is believed to occur not only in this band but to extend eastward and southeastward beyond the limits of the state. As for the Olmsted and the Huron, the former perhaps, the latter most probably, are thought to be confined to the west of the 81°30' meridian. Huron sedimentation may in fact be limited on the east by the crest of a low axis—the Carter axis—which is indicated across eastern Kentucky in a S. S. W. direction from Carter County, and from the same point in a generalized opposite direction through Ohio to the low arch shown along Lake Erie between Berea and Elyria. The Chagrin, on the other side, probably did not extend far to the west of the present crest of the same low arch. At any rate very convincing evidence must be offered before I shall admit that the Chagrin wedge reaches as far as Huron River. These relations are expressed graphically in fig. 1.

With the issue thus clearly set forth, namely, that there is no Chagrin shale in Huron County and no Huron beneath the Chagrin under Cuyahoga County, it is obvious that very rapid thinning of these formations must have taken place in the intervening area. The Chagrin, with a thickness of something like 1200 feet, must pinch out in 40 miles, or at the rate of 30 feet to the mile. The Huron overlapping eastward must lose approximately 300 feet in less than 30 miles. Is there sufficient warrant for such contentions in the records of deep wells in the affected area?

Comparison of published logs of deep wells in Ohio shows invariably a thinning of the shale complex in a westerly and north-westerly direction from Wellsville on the Ohio near the eastern border of the state. It shows, further, that the rate of pinching increases rapidly as it nears the Carter axis. Under Wellsville the shale complex is over 2600 feet thick, the bottom of the well being still in the shale. From this point to Huron River, a distance of something like 112 miles, the shale complex loses about 2000 feet, or nearly 18 feet per mile. To lose the whole of the 2600 feet would require thinning of a little over 23 feet per mile. The latter rate would be more nearly the proper one if we assumed that the shale under the Berea at Wellsville is, with the probable exception of perhaps 100 feet at Bedford, all pre-Huron Devonian. That it is late Devonian beneath the Bedford part is strongly suggested to my mind by the frequent presence of thick beds of red shale (presumably Catskill Che-

mung) in the wells at Bellaire and Wheeling from 400 feet on beneath the base of the Berea. But I shall not object if my statement that all of the pre-Bedford part in the Wellsville well is pre-Huron is for the present set down as pure assumption on my part. Whether the northwesterly thinning of the shale complex in this case is or is not confined to pre-Huron Devonian deposits is of no immediate consequence. Certainly it can have no vital bearing on the determination of a rate of overlap thinning in these formations that may be cited as a desired precedent. However the record is interpreted, the rate is not less than 20 feet to the mile; and that, considering the great distance, is ample for our purpose.

As I have said, the rate of thinning increases as we approach the Carter axis. As the first instance, I would cite the wells at Akron and Elyria. In the former the shale complex is at least 1737 feet (Orton, *Geol. Survey Ohio*, vol. vi, says 1862 feet), while in the latter it is but 800 feet. Here, then, the rate is a trifle under 27 feet to the mile. But much greater rates are recorded in the reports of the Ohio Geological Survey. I shall mention only three instances, the first two, as described by Bownocker,* occurring in the Lancaster-Bremen oil and gas field in the central part of the state, the third within the present limits of the city of Cleveland.† (1) In 25 miles due southeast from the Ruff well, No. 2, in the Pleasantville pool, to the Kennedy well, No. 1, the interval between the Berea grit and the Devonian limestone expands 110 feet (880 to 990 feet), making a rate of 44 feet to the mile. (2) In an east-west direction from Lancaster to the Lefever well southeast of New Lexington, a distance of 23 miles, the same interval increases from 630 feet to 1345 feet, that is, 715 feet, giving an average rate of increase of 31 feet per mile. In the first 9 miles, that is from Lancaster to Bremen, the increase is over 34 feet to the mile. Both of these instances lie on the eastern flank of the Carter axis. (3) This concerns differences noted in comparing the logs of the Newburg and Wade wells, the latter being located on Euclid avenue about 5 miles northwest of the former. Deducting differences in altitude of the well heads of the two wells, we find 1225 feet of shale in the Newburg well that is strictly comparable to 930 feet in the Wade well. According to these calculations, which have been verified by Professor Cushing, there is a difference of 295 feet in thickness of shale between the two wells. Dividing this by 5, the distance in miles between the two wells, gives nearly 60 feet of decrease per mile.

A low part of the Carter axis is indicated between Ashland

* Bownocker, J. A.: *The Bremen Oil Field*, Bull. No. 12, *Geol. Survey Ohio*, pp. 18-22, 1910.

† Orton, Edward: *Geol. Survey Ohio*, vol. vi, pp. 25-352, 1898.

and Mt. Vernon. In this area thinning of the shale complex is fairly uniform and does not vary much from 20 feet per mile. As will be noted, the rate continues about the same as between Akron and Wellsville. A few miles farther north, however, as between Lodi and New London, it advances to 30 feet per mile.

Taking the published records of wells to the west of a line connecting Cleveland, Lodi, and New Lexington, the average W.N.W. thinning of the shale complex seems not to be less than 30 feet to the mile. In places, as stated, it drops to 20 feet, in others it rises to 40 feet and even to more than 50 feet. Accepting 30 feet per mile as a fair average for north central Ohio, nearly the whole (over 1000 feet) of the 1116 feet of the shale complex beneath the town of Lodi will have disappeared before reaching the outcrops along Huron River, 34 miles away in Erie and Huron counties. That such thinning actually occurs in the first 19 miles of this distance is established by comparing the Lodi well, in which the shale complex is 1116 feet thick, with the well near New London, in which it is only 650 feet. Now, at the expense of which part, the top or the bottom, of the shale complex of eastern Ohio is this diminution taking place? In view of the unmistakable trend of modern stratigraphic geology, the possibility of the reduction being due to correspondingly varying rates of deposition seems so improbable that it need not be considered.

To begin with, especially since it is certain that we are dealing with overlapping formations, is it not quite reasonable to assume that the loss in thickness is by overlap thinning, hence from the bottom and not the top? Next, if we admit that the upper part of the shale complex under Lodi comprises beds referable to at least the Bedford and Cleveland shales, and most likely also beds corresponding to the recently named Olmsted shale, all three of which continue without break along the lake shore from west Cleveland to Huron River, it is clear that the fully demonstrated thinning of the shale complex affects only the beds beneath the Olmsted. More than that, Cushing shows that the Olmsted thickens westwardly along the lake from 0 in east Cleveland to approximately 100 feet at the western edge of the Berea triangle; in other words, this shale thickens westwardly, so far as followed, at the rate of about 6 feet to the mile. Should this rate of thickening continue westward to Huron River, an added distance of 26 miles, the Olmsted shale alone would there be something like 250 feet thick. But we know from outcrops studied by Newberry and Read, as described in the Ohio Survey reports on Erie and Huron counties, that both the Cleveland and the Bedford shales are represented in the highland rim of the Huron River valley by

total thicknesses ranging from 55 feet to 100 feet. The three formations, then, namely, the Bedford, the Cleveland, and the Olmsted, which are almost certainly represented in the shale complex under Lodi, would more than make up the balance left of the shale complex at Huron River after deducting its estimated westerly thinning of 1000 feet. In other words, the loss of 1000 feet between Lodi and Huron River, which leaves but 116 feet of the shale at the former place to be accounted for, would be much more than made up by the upper formations of the complex which we have every reason to regard as continuously developed between the two points.

It being plausibly established that the northwesterly and westerly thinning of the shale complex affects only its pre-Olmsted portions, we may now proceed to the consideration of the Chagrin and Huron divisions. I shall start with the assertion that west of the Carter axis a larger proportion of the shale complex belongs *above* the top of the Chagrin than is the case to the east of the mentioned axis; and this will presently end in the probable inference that practically the whole of the shale series usually referred to under the term Huron belongs *above*, and not beneath, the Chagrin.

That the assertion just made is founded on indubitable evidence becomes wholly clear when we recall the fact already mentioned that the Olmsted shale begins at West Cleveland to wedge in between the underlying Chagrin and the base of the typical Cleveland shale. As described, this wedge of distinguishable shale—the Olmsted of Cnshing—thickens steadily in a westward direction from Cleveland until its base sinks beneath the level of Lake Erie. To this point, however, it has added at least 100 feet to the post-Chagrin series of shales. Considering this fact in connection with the positively established rapid westward thinning of the underlying Chagrin, it is clear that orogenic movements resulting in reversal of direction of marine transgression had occurred in the interval between the close of Chagrin sedimentation and the beginning of the Olmsted. When did this reversal take place? May not the point where the Olmsted has attained a thickness of 100 feet mark only the middle or even some later stage in the easterly transgression that was superimposed on the westerly transgression of the Chagrin? That it does not mark the beginning of the reversal is proved to my conviction by the fact that this point is at least 20 miles to the east of the middle of the trough between the Carter and Cincinnati axes in which we may reasonably suppose that post-Chagrin deposition begun. It is quite reasonable then to assume that the Olmsted overlap is but one of the later stages of a marine transgression that began with the earliest of Huron deposition.

Between Cleveland and Sandusky there should be a point where the Chagrin is practically absent and where, therefore, the shale complex, minus the Bedford, is made up wholly of the Cleveland, Olmsted, and such part of the presumably likewise overlapping Huron as may have reached there. This place would seem to be near the mouth of the Vermilion where Newberry* reports a well as showing "the thickness of the shales which separate the Berea grit from the Sandusky (Delaware) limestone to be less than 400 feet."

The foregoing interpretation of the relations of the Chagrin and the Huron (see also figs. I-III, p. 166) will seem less strange when it is remembered that decided changes in the direction of marine invasions occurred also at other times in the areas under discussion during the Silurian, Devonian and Waverlyan. Thus it may be said to be established that the Onondaga invaded from the south while the late Devonian faunas came in chiefly from the east, only one of the latter, the Lime Creek fauna of Iowa, having extended eastward to New York from the west. Further, it seems undeniable that all of the Chattanooga black shales came in from the south while the Bedford probably invaded Ohio from the southeast. In other ages finally Atlantic seas that transgressed westwardly or northwestwardly across eastern and northern Ohio alternated with seas that came in from other oceanic basins, and advanced in approximately opposite directions. Such oscillations and resulting changes in direction of marine transgression in the continental basins are really of very common occurrence in geological history.

Fossil evidence.

Finally a few words concerning the faunal aspects of the Chattanooga shale problems. As I have already said in remarks following the preceding description of the formations involved in this discussion, it seems unnecessary to enlarge on the fauna of the Chagrin formation. After saying, as all have who have studied its fossils, that they can not be older than Portage and are most probably Chemung, it might be sufficient to add that under the stratigraphic arrangement here proposed the Chemung affinities of the Chagrin fauna may justly be emphasized. But I shall further add that the probable presence of an unquestionable species of *Syringothyris* in the upper part of the formation,† if it is used at all, must

* Geol. Survey Ohio, vol. ii, p. 216, 1874.

† The occurrence of *Syringothyris* in the Ohio section beneath the Cleveland has recently been denied. However, some well-preserved specimens of a new species of this genus, collected near Jefferson in Ashtabula County, from beds regarded as older than the Cleveland by such good authorities on Ohio stratigraphy as Professors H. P. Cushing and Charles S. Prosser (information contained in letters to the writer) seem to revive the asserted

be cited as evidence tending to prove that the top of the Chagrin is in places at least not older, if indeed it is not slightly younger, than the highest beds of the Chemung in Pennsylvania and New York.

Supposed Genesee fossils in the basal part of the Ohio shale.—Fossils which have been compared or identified with species found in the Genesee shale of New York have been frequently listed and described as from the basal part of the Ohio and New Albany shales. I do not wish to deny that fossils having such affinities occur in these black shales. Indeed I have often seen them there. But I do wish to recommend caution in correlating all such occurrences as Genesee. The age relations of black shale faunas generally are notoriously deceptive. If space were available I would cite several most instructive examples. The precedent of these fully established cases of persistence of black shale faunas—in two instances proving a range from well down in one system to a position well up in the next—would fully warrant throwing out as inconclusive all the fossil evidence yet cited from the Chattanooga series as indicating the Genesee age of the beds from which such fossils were procured. But I am not inclined to do this at the present time. I am only recommending caution and close inspection of not only the specimens but also of every kind of evidence that may be used in stratigraphic correlation before it is decided that any *Linguloid* or any *Leiorhynchus*, *Prioniodus*, or *Sporangites* is really the Genesee occurrence of the species to which they seem to belong and not some later or earlier occurrence of the same.

Is there any warrant for citing the "Huron" fauna and flora as Devonian?—I wish to ask, how came the Huron fossils to be called Devonian? The answer is obvious enough when we consider that the beds containing them were, as I believe, erroneously regarded as underlying the Chagrin with its undeniably Devonian fauna. Under this probable misconception the Huron fishes in particular were, without evidence of their own, simply referred to the Devonian column as soon as each was discovered. I am aware, of course, that for more than sixty years most geologists correlated the black shale of Kentucky as Genesee or earlier; but there were also others who held a different view and made it younger. So after all it was not until the Ohio geologists placed the Chagrin above

presence of this—otherwheres in the Ohioan province, strictly Waverlyan—genus in beds underlying the Cleveland shale, on a firmer basis than heretofore. But it is to be understood that these Jefferson specimens have nothing to do with those mentioned many years ago by Newberry as having been found in a similar position at Bedford. All agree now that the latter came out of some Bedford float which had gone down stream.

the Huron that a Devonian and perhaps Genesee age seemed assured for the latter.

Since reaching the conclusion that the Chagrin really belongs beneath and not above the Huron, I have searched the literature and found but a single unqualified identification of an unquestionably Devonian fish in a Chattanooga formation, namely, *Dinichthys pustulosus* Eastman. But this species is said by Eastman* to range throughout the middle Devonian of the Mississippi Valley as well as in the Oneonta beds of New York and the Chattanooga shale in Kentucky. Very likely the identification is at fault in the latter two cases. *Dinichthys curtus*—a Cleveland shale species—is doubtfully reported by Newberry from supposed Chemung beds in Pennsylvania. All other species referred to by Eastman in his memoir on fossil fishes of New York as common to the Cleveland shale and the Devonian of New York have been identified solely by means of fragmentary material, very possibly under unconscious influence of preceding belief in the general contemporaneity of the beds.

Fossil wood of the type of *Dadoxylon newberryi* occurs in the Genesee of New York and has been identified specifically with this Ohio shale fossil. But it would be no difficult matter to fall into error in the identification of these fossil woods when the preservation of the specimens is not unusually good. Besides, a piece of wood that is externally at least very much like *Dadoxylon newberryi*, though differing appreciably in minute internal features whose importance I am not qualified to judge, has been found in southwestern Missouri at the base of the Fern Glen, which I regard as early Osagian in age. Perhaps this specimen should be viewed as a boulder from nearby Chattanooga shale. Fairly good remains of plants allied to *Calamites* also have been found in both the Huron and the Genesee. Specific identity has been claimed for these, but I am not satisfied that the case has been proved. Until the specimens have been critically compared by a thoroughly competent observer like Mr. David White, who is now engaged on their study, I prefer to remain silent respecting the proper interpretation of the evidence afforded by these and the other plants involved in our problem.

Similarity of the Huron and Cleveland shale formations.
—The close and constantly growing agreement between the faunas of the Huron and Cleveland shales in Ohio has recently been emphasized by Kindle in his endeavor to prove the Devonian age of the Cleveland. Obviously, in view of my contention that these two shales are but members of a single diastrophically determined stratigraphic unit, entirely subse-

* Eastman, C. R.: Memoir 10, New York State Mus., p. 133, 1907.

quent in age to the Chagrin, I welcome every bit of evidence that he may bring toward proving their faunal unity. In fact, I regard this strong faunal agreement as the most important feature of the deductive part of the evidence on which the views herein advocated are based.

Summary of conclusions.

(1) I contend that the fishes and other fossils commonly credited to the Huron shale of Ohio have never been and, as I believe, can never be shown to be really of the age of the upper Devonian of New York. Their common acceptance as *bona fide* Devonian fossils rests solely on the unproven and probably mistaken belief that the beds in which they are found are older than the Chagrin, which is unquestionably upper Devonian. If the Huron is as I claim younger, then its fossils can not be really Devonian species unless the boundaries of this system are expanded upward beyond the limits of the New York standard.

(2) Regarding the Chagrin I claim that this formation has been unquestionably recognized in northern Ohio only to the east of Lorain County. In this stretch there is no difficulty whatever in drawing the boundary between the Chagrin on the one side and the Olmsted and Cleveland on the other, so long as the latter two continue to be represented in the section. The contact between the Chagrin and the other two in this stretch seems, moreover, to be unconformable by overlap and to mark a stratigraphic hiatus of considerable importance.

Regarding the beds to the west of Avon, or of some other point in Lorain County, that have been referred to the horizon of the "Erie" or Chagrin, I contend that the evidence for such reference is in every case undecisive; in most it is clearly open to question, and in others already disproved. (Vide Newberry, U. S. Geol. Survey Monog. xvi, 1889, p. 127, where he corrects an error and states that "none of the fossil fishes described from northern Ohio should be credited to the Huron," and "that all the outcrops of black shale (along the lake shore) in Cuyahoga and Lorain counties belong to the Cleveland (more likely Olmsted) shale.") So far as I can see, there is no break in the Huron-Cleveland section in Huron County and certainly none between that small middle part of the section which is referred to as "Erie" by Read and others, and that upper portion which they doubtless correctly recognize as Cleveland. If these correlations by Newberry and Read were correct, the absence of a break at the latter horizon would be most extraordinary in view of the fact that a break is clearly indicated to the east of Lorain County between the true Chagrin ("Erie")

and the Cleveland. The absence of a break at the base of the Cleveland in the Huron County section is, therefore, regarded as strongly corroborative of my claim that there is no "Erie" or Chagrin in the middle part of this section; and that the whole of the black shale series here, beginning with the *Dinichthys herzeri* zone and ending with the top of the Cleveland, is in fact a wholly distinct, single, though lithologically tripartite, formation, thickening westwardly from Cleveland and pinching out entirely in the opposite direction near the Pennsylvania state line.

The full significance of Newberry's admission that the Chagrin thins rapidly westward from Cleveland and that all the black shale outcrops in Lorain County are of Cleveland (including Olmsted) shale has not been appreciated. This admission, if it does not fully establish, at least renders it highly probable that the Chagrin is wholly unrepresented in the outcrops of the black shale series (including the "Huron") to the west of Lorain County. The general unity of the Huron-Olmsted-Cleveland zones, or rather the unbroken stratigraphic record presented by them, is further strongly indicated by the general similarity of their fossil contents. This similarity in types is growing more obvious year by year. The Conodonts show very little differentiation from the Huron on to the Sunbury and some of the true fishes even are being found common to the Huron and Cleveland. Take whatever line of evidence we may, there is no positive and little negative evidence indicating that the Huron is not merely the basal member of an unbroken depositional record in north central Ohio, of which the Cleveland shale constitutes the upper member.

(3) With the disproof of the probably mistaken belief that the Chagrin belongs above the Huron, the main reason that caused Orton to view the black shale series in central Ohio as representing all three shales—the Huron, the Erie, and the Cleveland—and those other reasons which influenced Prosser and many others in reaching the conclusion that only the Huron is represented in the Franklin County section—all these diversely interpreted reasons disappear. We have, then, in Franklin as in Huron County, also in the southern part of the state, an Ohio formation comprising a Cleveland shale member above and a "Huron" (or whatever it may be called) member beneath, with an unnamed middle member locally distinguishable between them.

(4) This new conception does not introduce an extraordinary condition. Much of the same kind of distribution of stratigraphic units occurred in northern Ohio during the Silurian. This is seen from comparison of wells at Cleveland and Sandusky. At the latter point we find 970 feet of Silurian

limestone (chiefly) beneath the Onondaga limestone; at the former there are, according to Orton's interpretation, all of 1,600 feet of limestone and salt beds belonging in the same interval. Moreover, analysis of the records indicates that beds of great thickness in either well are either thin or entirely absent in the other. In the Silurian and early Devonian, as in the late Devonian and Waverlyan ages with which this discussion is chiefly concerned, the waters invaded alternately from the east and south, or possibly north, and the deposits of each overlap and finally pinch out in the direction of the invasion.

(5) This new interpretation of the "Devono-Carboniferous shale problem" seems to me to have great advantages over those hitherto suggested. In the first place, it offers a much more simple and, may I say it, rational correlation and classification of the stratigraphic units involved. Next it does away with that uncertainty (connected with the identification of the assumed Chagrin element in the middle part of the series) which has been so prominent a feature of the problem heretofore. It substitutes sharp diastrophic boundaries between the upper Devonian Chagrin and the overlapping base of the Chattanooga series for assumed and difficultly placeable transitions, and it does away with the necessity of explaining how a sharply defined series of alternating gray and black Devonian shales, that maintains its lithologic characteristics from central Pennsylvania to Cleveland, could yet change its character materially in the next 40 to 50 miles to the west from Cleveland. Third, it makes an essential unit of two faunas whose likeness has been generally recognized—and is in truth undeniable—but which have hitherto been conceived as widely separated by a thick series of upper Devonian beds holding a very different fauna. Finally, it ascribes the local variation in stratigraphic sequence chiefly to differential oscillation and invasion of distinct seas and to consequent overlap in different directions of deposits representing the several invasions, and only to a very limited extent to variations in kind and rate of deposition.

ART. XVII.—*Pseudomorphs after Stibnite from San Luis Potosi, Mexico*; by W. E. FORD and W. M. BRADLEY.

RECENTLY the Brush Mineral Collection acquired from the Scott Mineral Company of New York City an interesting crystal which, on study, proved to be a pseudomorph after stibnite. Through the courtesy of Mr. Scott two other crystals were placed at the disposal of the writers for study, and sufficient material was donated for an analysis. As no stibnite pseudomorphs as large or as perfect as these have been previously known, it was felt that a brief description would be of interest.

The specimens are found about ten miles to the west of Charcas, San Luis Potosi, Mexico. They occur in small veins which traverse a limestone. In the majority of cases the long prismatic crystals cross the veins from wall to wall and are consequently unterminated, but occasionally, when the vein cavity enlarges, well-developed crystals are found.

The three crystals studied averaged 10^{cm} in length and varied from 1 to 2^{cm} in thickness. The prism zone on the crystals was deeply grooved and striated in a vertical direction, but in places the different faces occurred with sufficiently wide and smooth planes to admit of their identification. In each case only one-half of the faces of the terminating pyramids were developed. Because of the dull, earthy luster shown by the crystals, measurements could only be made with a contact goniometer. The faces, however, were smooth enough in character and sufficiently large to permit of reasonably accurate measurements. In this way the presence upon the crystals of the following forms was determined: $b(010)$, $n(210)$, $m(110)$, $o(120)$, and $\tau(343)$. On the crystal represented in figure 3 two faces of a second pyramid were observed, which, however, could not be identified with any known form of stibnite. The faces of this pyramid were small but of good enough quality to insure contact measurements that would be accurate to within one or two degrees. The angles measured between the two faces of this pyramid, and between them and the prism faces, were always within a degree of the calculated values for a form having the symbol (6.10.15). But the character of the faces and the fact that they were observed on only one crystal must leave the identity of this form in doubt.

The material of which these pseudomorphs are composed is fine-grained in texture and of a pale, dirty yellow color. When finely powdered and immersed in Canada balsam, it appears of uniform character under the microscope. The larger grains were quite opaque, and only the smallest particles were trans-

parent. These proved to be isotropic, and since they showed no evidences of crystal form or cleavage, the mineral is probably amorphous in character.

FIG. 1.

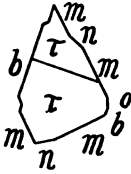


FIG. 2.

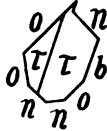
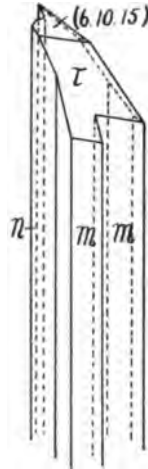
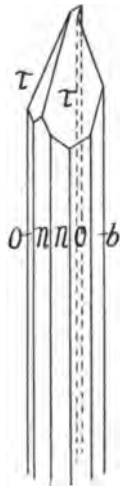
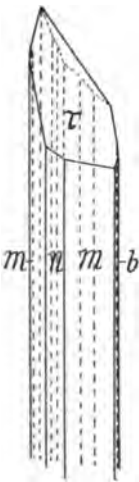
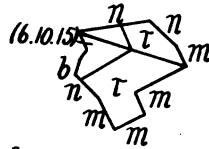


FIG. 3.



It was at first thought that the material of the pseudomorphs would prove to be a simple antimony oxide, perhaps cervantite. But the analysis showed, however, that notable amounts of water and lime were present. The method of analysis was briefly as follows: The finely powdered mineral was thoroughly fused with sodium carbonate. This fusion was dissolved in hydrochloric acid, and the antimony precipitated as the sulphide by hydrogen sulphide gas. The precipitate was collected on asbestos in a filter tube, ignited in a current of hydrogen sulphide, and weighed as Sb_2S_3 . The calcium was precipitated in the filtrate by ammonium oxalate, and weighed as CaO . The water was determined by ignition, and in one case this result was checked by making a direct weighing of the amount of water set free when the mineral was ignited in a closed glass tube. During the analysis the absence of MgO , Al_2O_3 , and SiO_2 , was proved.

Two complete analyses and one partial analysis were made of one sample, which consisted of small crystal fragments. The results were as follows :

Specific gravity, 4.906.				
	I	II	III	Average
Sb ₂ O ₃	85.43	85.64		85.53
CaO.....	9.64	9.69	9.81	9.71
H ₂ O.....	4.84*	4.83*	4.73†	4.80
<hr/>				
Total.....	99.91	100.16		100.04
* Loss on ignition. † Direct determination.				

It happened that this analysis yielded quite definite molecular ratios. The formula, however, which was derived was quite unusual and was very different from that of any known antimonate. It was thought, therefore, that the ratios might be accidental, and a second analysis was made in order to decide this point. The second sample was taken from the lower end of one of the crystals, and the results of its analysis follow :

		IV
Sb ₂ O ₃		90.43
CaO.....		7.36
H ₂ O.....		3.83
<hr/>		
Total		101.62

By the comparison of the analyses of the two samples it will be seen that the composition is not uniform, and so, consequently, no definite formula can be assigned to the material. In the analysis the antimony has been calculated as the pentoxide, but the question of the state of oxidation of the antimony is a difficult one to decide. The fine powder of the mineral was partially soluble in hydrochloric acid, and this solution contained antimonous antimony since it liberated iodine from a potassium iodide solution. Since the mineral is only partially soluble in hydrochloric acid, and in view of the fact that when the antimony found in analysis IV is all calculated as Sb₂O₃, the summation of the analysis shows an excess, the assumption is natural that the mineral contains the lower oxide, Sb₂O₃, as well. Further, if the mineral contains Sb₂O₃ in the usual form it should liberate oxygen when ignited, being reduced to Sb₂O₃. That this does not take place is proved by the agreement between the determinations of water made by the two different methods. The conclusion arrived at is that the mineral is not a definite compound, but is composed rather of amorphous material with varying composition.

Mineralogical Laboratory of the Sheffield Scientific
School of Yale University, New Haven,
June 1st, 1912.

ART. XVIII.—*The Stratigraphic Relations of the Devonian Shales of Northern Ohio*; * by EDWARD M. KINDLE.

Introduction.—Northeastern Ohio is an area of unusual importance to students of late Devonian and early Carboniferous formations and faunas. An acquaintance extending over several years with the border land of Devonian-Carboniferous stratigraphic paleontology in the Allegheny region and the states adjacent to Ohio has resulted in the conviction that northeastern Ohio affords a better opportunity for a satisfactory discrimination and placing of the boundary between the Devonian and Carboniferous than any other area in the eastern states. Here we are not confronted with a great series of nearly barren beds in the vicinity of the base of the Carboniferous as we are in southeastern New York and in much of the Allegheny region. Neither do we have to deal, as in southern Kentucky† and Tennessee, with a set of formations so nearly alike on the two sides of the boundary as to make discrimination sometimes difficult. On the contrary, the formations of the late Devonian and early Carboniferous show very marked lithologic differentiation in northeastern Ohio. Reference to a properly established point is of no greater importance to the engineer than is the selection by the stratigrapher of a horizon whose relative position can be fixed with precision in the general time scale. Northeastern Ohio is, therefore, a favorable region from which to approach the difficult problems of the stratigraphy of the black shale formations of the Ohio shale group. The geologist can start here with a horizon for a reference plane which is marked not only by the diverse lithology of the Bedford shale and the Berea sandstone, but by an unconformity separating the two. At present this appears to be the only horizon between the Devonian limestone and the Carboniferous which all geologists agree extends uninterruptedly across northern Ohio from the Pennsylvania line almost to the Devonian limestone belt south of Sandusky. Its position on the map (fig. 1, p. 190) is shown approximately by the line separating the Ohio shale area in outcrop from that under cover. This definitely-marked horizon above, and the even more conspicuous boundary at the top of the Devonian limestone below, mark the limits of the formations with which we are concerned in this discussion.

* Published with the permission of the Director of the U. S. Geological Survey.

† Limitations of space make it desirable to defer the further discussion of the age of the Chattanooga shale to another paper. For critical review of the evidence on record see this Journal, Feb., 1912.

Quite recently* a new hypothesis concerning the relations of the lighter and darker colored shales of the Ohio group has been advanced by Mr. E. O. Ulrich which requires consideration in the present attempt to present the writer's observations on these terranes in Ohio. This hypothesis assumes that the black shale formations of the Ohio group—Cleveland and Huron—overlap on the light-colored Chagrin shale instead of including it between them, as heretofore held by all geologists who have studied these beds. (See fig. 3, p. 204.) The interpretation of northern Ohio stratigraphy presented in Mr. Ulrich's paper† is an entirely novel one, and if it should prove to be also true, a most important one. It merits, therefore, a careful examination. If we are to have a science of stratigraphic paleontology we must not accept either plausible explanations or good guesses without critical examination. We can not, of course, accept without scrutiny Mr. Ulrich's preliminary assumption that "since it is certain we are dealing with overlapping formations,"‡ etc. If we should take this as our major premise without first demonstrating its truth, it is possible that our conclusions would bear much the same relation to the facts as did those of the medieval geographers who started with the dictum regarding the surface of the earth, that "it is certain that we are dealing with a flat plain." In the course of presenting some of the results of the writer's observations on the stratigraphy of the Ohio shale group, it is proposed to test Mr. Ulrich's theory by ascertaining whether it will fully fit the facts, both new and old, which are now available concerning the Ohio group. If it will accommodate all of the data concerned, it will then be in order to consider whether it does so more perfectly and has a greater or less degree of probability than the conception which has hitherto been held regarding the relations of the terranes known collectively as the Ohio shale before we can decide which is to be discarded. Before taking up this specific problem it will be worth while to get as clearly as possible Mr. Ulrich's general viewpoint on stratigraphic problems. By so doing we shall see that the theories which he has applied to the Ohio shale group are legitimate deductions from some of the general propositions advanced in his work on *Revision of the Paleozoic Systems*.§ The one which is most pertinent to the case in hand is the doctrine of the "geographic persistence of lithologic units."|| The very wide or universal extent of a given kind of sediment within the limits of any Paleozoic sea is a rather fundamental part of Mr. Ulrich's system of diastrophic corre-

* Paper presented before the Geol. Soc., Washington.

† Read before the Geol. Soc., Washington, Feb. 24, 1912; see also the paper in this number of the Journal.

‡ Idem.

§ Geol. Soc. America, vol. xxiii, 1911.

|| Idem., p. 318.

lation. This conception is rather closely akin to, if not a direct lineal descendant of, Werner's old idea of "universal formations." Ulrich has himself called attention to the fact that this view is widely at variance with the principles of sedimentation laid down in such standard works as Geikie's, Kayser's, and Dana's text-books of geology, and has taken exception to Dana's rather axiomatic statement that "many a sandstone in New York and Pennsylvania is of contemporaneous origin with a limestone in the Ohio and Mississippi valleys." It may be added that Mr. Ulrich's views on this subject are equally at variance with the opinions of nearly all stratigraphers. Most stratigraphers agree that the lateral variations of sedimentary deposits are neither slight nor negligible. Although nowhere explicitly stated, it is the reverse of this proposition which forms the major premise in Mr. Ulrich's discussion of the Ohio group stratigraphy. If, as this assumption indicates, the sediments of any Paleozoic sea were essentially the same from center to shore, then a gray sandy shale such as the Chagrin of northeastern Ohio could not possibly be synchronous in time with the finer-textured black shales in the adjacent parts of Ohio to the westward. This major premise, if admitted, would of course require the assumption of axes and distinct ocean basins to account for the juxtaposition of apparently synchronous deposits of diverse lithologic type such as we find in the paper under discussion. Concerning the soundness of this fundamental assumption regarding the "persistence of lithologic units," it must suffice here to refer the reader to the authorities cited above and to his own knowledge of the very wide diversity of sedimentation now in progress in nearly every lake and sea, regardless of the relief of adjacent lands.

The maintenance of the doctrine of the "persistence of lithologic units" has led Mr. Ulrich to make a far more extensive application of the overlap hypothesis in treating problems of correlation than any other author has permitted himself to make. The overlap theory is of course in some cases a demonstrable fact; in others, where only one or two or a very few of the important facts are known, it often appears at first to be a satisfactory explanation, but with access of knowledge it in many cases becomes inadequate. It is very easy to pass a straight line through any two points but it may be impossible to make it touch a third, and so with Mr. Ulrich's application of the overlap hypothesis. When he attempts to make it cover only two facts in the case, namely, deposits showing lithologic and faunal differences and having a different areal distribution, no difficulty is found in adjusting it to any such case where other data are wanting, but when the attempt is made to fit it to various other facts which must also be accounted for it may

entirely fail. In the succeeding discussion we shall see to what extent the application of the overlap theory to the shales of the Ohio group, and their consequent separation into formations originating in distinct seas and belonging to different

FIG. 1.



FIG. 1. Map of the Ohio shale group after Professor Orton. Line A-B indicates approximate position of sections shown in fig. 3.

systems, affords an adequate explanation of all the facts which are known about them.

The overlap hypothesis.—The grounds on which the overlap theory rests as applied to the Cleveland and Huron shales will now be considered. Inspection of the accompanying map by Prof. Orton* of the Ohio shale group, figure 1, will aid the reader in following the discussion. The theory proposed by Ulrich assumes that the portion of the Ohio shale group called

* Geol. Surv. of Ohio, vol. vi.

the Chagrin shale which as a surface formation lies mainly east of Cleveland, originated in a sea older than and distinct from the one in which the darker shales of the same group west of Cleveland were deposited. The advocacy of this hypothesis appears to rest essentially on two kinds of evidence. These briefly stated are (1) faunal and lithologic differences between the shale of northeastern Ohio and the shale of the Huron River region and (2) discordance in direction of dip between the Cleveland shale and the Devonian limestone base of the Ohio shale group. These facts of course are not new. Newberry, Orton and others who considered the Chagrin and the black shales to the westward synchronous deposits were doubtless familiar with them owing to their intimate acquaintance with the geology of Ohio. We have, therefore, to consider only a new interpretation of well-known facts.

We may inquire, first, whether the differences in the kind and amount of organic remains which distinguish the fauna found in the Chagrin from that in the Cleveland and Huron shales are of such a character as to indicate that the two faunas lived in distinct seas, as the overlap theory assumes. Paleontologists who are familiar with the work of marine zoologists know that in the present seas a particular fauna may be found to follow the coast-line within the limits of shallow coastal waters for hundreds of miles and yet disappear completely in deeper water a few miles to seaward off any part of the coast. The bathymetric limitation of faunal distribution is a fact of the utmost importance to the paleontologist and one too often lost sight of when differences in faunas are offered as evidence of overlap and distinct age. Risso, the naturalist of the seas of Nice, was perhaps the first to call attention to that distribution of marine life which is dependent upon depth. Goodwin-Austin has concisely stated this principle of the distribution of marine life in the following words:

"The sublittoral zone of every sea and ocean presents the fullness of its fauna and from that it decreases progressively and rapidly"

A good specific illustration of the general principle is given by Jeffries† from the Mediterranean Sea. In the Bay of La Spezia, in the eastern Mediterranean, Mr. Jeffries, after describing the rich and varied fauna at slight depths, continues: "For several leagues seaward in from fifteen to forty fathoms I met with nothing but tenaceous mud with *Turritella communis* and a curious variety of *Calyptrea sinensis*." Here we find in the eastern Mediterranean a molluscan fauna, which,

* Goodwin-Austin, Robert: Nat. Hist. of European Seas, 1859, p. 246.

† Nat. Hist. of European Seas.

according to Forbes, numbers about 500 species, reduced in the vicinity of La Spezia, with increase of the depth of the water amounting to no more than 120 feet, to one or two species. Jeffries's account of the rapid disappearance seaward of the rich molluscan fauna of La Spezia is very similar to that which the paleontologist must give of the faunal changes which he encounters in passing westward from Ashtabula County, Ohio. There the rich molluscan fauna of the Chagrin shale in the Jefferson region is represented in every section by thousands of shells belonging to many species and genera. Thirty miles west of Ashtabula County the same gray Chagrin shale of the Cuyahoga River valley holds a comparatively sparse fauna. Still farther west, 15 miles, the Chagrin shale in the Rocky River section is almost if not entirely barren of invertebrate fossils. In the basal beds of the Cleveland shale, into which the Chagrin grades laterally as shown in figure 3, p. 204, a rich fauna of conodonts and great fishes occurs, some of the latter having had a length of 20 feet or more. In the sections to the west of Rocky River the fauna of the Chagrin shale is represented only by an occasional *Paleoneilo* or other rare mollusc, while conodonts and the remains of great fishes occur throughout the dark shales which, in this westerly region, have been held to represent the lighter-colored Chagrin shale. No one, we believe, who is familiar with the work of such naturalists and geologists as Edward Forbes, Jeffries, and Walther will deny that the great faunal changes briefly outlined above, which are found in following the Ohio shale westward from the Pennsylvania line, are such as might be expected in following a fauna in a line normal to the direction of its bathymetric facies. It will be instructive to give here a brief summarized statement of the observations of Edward Forbes on the zonal distribution of the marine life of the British seas for comparison with the very similar zonal distribution which characterizes the fauna of the Ohio shale.

"British marine animals and plants are distributed in depth (or bathymetrically) in a series of zones or regions which belt our shores from high water mark down to the greatest depths explored. The uppermost of these is the tract between tide marks; this is the Littoral zone." *Littorina*, *Mytilus*, and *Fusus* are the dominant forms of this zone. Below low water mark these mollusca give way to other shells. The next or Laminarian zone extends to a depth of about 15 fathoms. In this zone grows the gigantic species of seaweed called *Laminaria*. Among these live myriads of shell fish and other forms of life. The genus *Lacuna* among the mollusca is especially characteristic of this zone. From 15 to 50 or more fathoms the majority of the inhabitants are predaceous. "Many of our larger fishes belong to this

region, to which on account of the plant-like Zoophites abounding in it the name coralline zone has been applied.”*

If the sea-bottom fauna thus described by Forbes were elevated and the entombed remains of the Laminarian and coralline zones of the Irish sea should be studied by paleontologists, some of them would doubtless assert, as they do of the Cleveland and Huron shales, that “it is certain that we are dealing with overlapping formations” in the deposits of the coralline zone. In a general way the fauna of the Chagrin shale in northeastern Ohio bears a relation to that of the Cleveland and Huron shales very similar to that which the Laminarian and coralline zones sustain to each other in the British seas. Corresponding to the Laminarian zone, rich in seaweeds and shell fish, there is in the Chagrin of northeastern Ohio a very populous molluscan fauna associated with the impressions of great numbers of seaweeds. Farther west, where these have disappeared, we find the great predatory fishes of the Cleveland and Huron shales which appear to have represented the dominant forms of life in the deeper parts of the Ohio Devonian sea just as large fishes are said to do in the present British seas.

The foregoing discussion indicates the analogous character of the differences existing between the faunas found in different areas of the Ohio group and those which distinguish two of the faunal zones of our present seas. The futility of attempting to use such differences as evidence of distinct and overlapping sea deposits becomes quite evident after these facts have been pointed out.

There remains still to be considered the rather marked lithologic differences which distinguish the Chagrin from the Cleveland and Huron shales. Could the fine-textured black carbonaceous shale found between Cleveland and Sandusky have been deposited in the same sea at the same time as the light colored sandy Chagrin shale of northern Ohio? If Ulrich's doctrine of the “persistence of lithologic units” is true, they can not be synchronous deposits and they must be successive or overlapping formations. Let us examine this doctrine in the light of some of the observations which have been made on the processes of sedimentation now in operation. Tyndall's† observations on the varying amounts of suspended matter in the sea water at different points off the southwestern coast of Europe are pertinent to this question. He found the amounts of suspended matter in the sea water to differ widely at different points. Sometimes the change was abrupt, as at a point 14 miles off Cadiz harbor: “Here there is a sudden

* Forbes, Edward: On researches into the natural history of the British seas; Edinburgh New Phil. Jour., vol. 1, pp. 335-339, 1851.

† Tyndall, John: Fragments of Science, pp. 127, 128.

change from yellow-green to a bright emerald-green, and accompanying the change a sudden fall in the quantity of suspended matter." Again, he notes the sharply defined limits of the normal Mediterranean waters and the Atlantic current which sets into the Mediterranean: "On the one side of it the water was a vivid green, on the other a deep blue. Standing at the bow of the ship, a bottle could be filled with blue water, while at the same moment a bottle cast from the stern could be filled with green water." It is of course obvious that the amount and kind of sediment which accumulates at any point on the sea bottom will depend largely upon the quantity and kind of suspended matter in the sea water above it.

The sharp contrasts in the type of deposits which we find at present forming around the coasts of the Gulf of Mexico may be cited here as bearing on the question of the "persistence of lithologic units." Off the mouth of the Mississippi River immense deposits of argillaceous mud are being deposited. The mud brought down by the Mississippi River can not, however, be detected beyond "about 100 miles from the Passes."* A few hundred miles to the eastward of the Mississippi in the Florida-Bahama region we find vast areas of chalky mud. Vaughan's† work on the Florida coast has shown that the bottom deposits now forming inside the Florida Keys vary from quartz sand to nearly pure calcareous ooze. Thus we find various kinds of deposits are now forming in different parts of the Gulf of Mexico. The whole continental platform from Long Island to Hatteras off the east coast of the United States is so swept that, according to Willis,‡ sand alone comes to rest, all finer sediments being carried to deeper waters.

The systematic examinations of the bottom deposits of the Irish sea have shown that it is characterized by a wide diversity of sediments. Clean sand and mud and clay are prominent among these and have distinct areas of distribution.

"Clean sand covers the floor generally in the shallow water of the eastern area between the Isle of Man and Lancashire where the depth does not exceed 10 fathoms . . . Mud and clay may be deposited in shallow water under special conditions, but it is principally found in the deep gully lying west of the Isle of Man at depths of 50 fathoms and over."§

The bionomic conditions and the character of the bottom deposits of the Black sea as revealed by the researches of

* Agassiz, A.: *Mus. Comp. Zool.*, vol. xiv, p. 128.

† Vaughan, Thomas Wayland: A contribution to the geological history of the Floridian plateau, Carnegie Institution of Washington, Publication 133, p. 119, 1910.

‡ Willis, Bailey: *Principles of Paleogeography*, Science. n. s., vol. xxxi, p. 19, 1910.

§ Herdman, W. A. and Lomas, J.: On the floor deposits of the Irish sea, *Proc. Liverpool Geol. Soc.*, vol. viii, p. 215, 1897.

Andrussow* have deep significance in connection with the interpretation of the marine conditions which produced the diverse faunas and stratigraphy of the Ohio shale. Their interest in this connection suggests the introduction here of a portion of Clarke's† quotation of Pompeckj's‡ observations on the Black sea:

"The sediments of the black sea are: (1) in the littoral zone and to a depth of about 20 fathoms, accumulations of sandy detritus; (2) to the 100 fathom line, gray blue sticky mud, from 35-100 fathoms, rich in *Modiola phaseolina*, etc.; (3) in the great depths the bottom is covered with (a) very fine, sticky, black mud with rich separation of FeS, abundant remains of planktonic diatoms and with fragments of quite young lamellibranchs (early stages of widely scattered plankton forms, (b) dark blue mud; FeS is here in less measure, but in richer quantity are separations of minutely grained CaCO₃, making at times thin banks; skeletons of pelagic diatoms are also abundant."

From these observations it appears that the Black sea furnishes an example of black sediments now forming in its deeper parts which are essentially like those of the Cleveland and Huron shales. The accumulations of sandy detritus in the more shallow parts of the same sea represents a type of deposits similar to the Chagrin shale.

We pass now to a brief consideration of the second class of evidence on which the overlap theory rests, namely, the present relative attitude of the dark shales and the underlying limestone. The Cleveland shale and the Devonian limestone at the base of the shale series show a gentle dip in opposite directions, the latter toward the Allegheny region, the former away from it. The interpretation placed by Ulrich on the diverse declinations of the Cleveland shale and the Devonian limestone is that the former represents a marine basin entirely distinct from the one in which the shale following the Devonian limestone in eastern Ohio was laid down. Opposed to this interpretation, however, there is a well established and universally accepted fact. If there is any general fact regarding the Devonian shales which is better attested than others in eastern Ohio, it is the rapid thickening of the series in passing eastward toward the Allegheny region. Hence, it follows that unless the easterly declination of the basal floor of Devonian limestone is more rapid than the rate of thickening of the shales, the con-

* *La Mer Noire: Guide des excursions du 7 Congrès géol. internat.* 1897, No. 29.

† Clarke, John M.: *Naples fauna in western New York*, New York State Mus. Mem., vi, p. 201, 1904.

‡ Pompeckj: *Die Jura-Ablagerungen zw. Regensburg und Regenstauf* (Separate from *Geognost. Jahresheft*, 1901, 14 Jahrgang, p. 43 et seq.)

tact planes of its upper members will show a westerly declination. Such westerly declination consequently can not be admitted as evidence for the overlap theory. While both the theory of the synchronous origin of the Huron and Cleveland of the Huron River section with the Chagrin, and the theory of the Cleveland shale overlap adjust themselves equally well to the westerly dip of this shale, another and most important fact fails to find a place in the latter theory. The Cleveland and Chagrin shales, unless the observations of the writer are at fault, are conformable. They must therefore represent successive deposits in the same sea. Since unconformity between the two has been assumed by Mr. Ulrich and is necessary to his theory, the evidence against this assumption will be presented in some detail on later pages in the discussion of the stratigraphy.

Stratigraphy of the Ohio shale group.—The Ohio shale group as defined in the reports of the Ohio Geological Survey comprises three formations. These in descending order are the Cleveland, Chagrin, and Huron shales.* The reader is

* Note:—A fourth member of this shale series has recently been proposed by Prof. H. P. Cushing (this Journal, † p. 583) under the name of the Olmsted shale. The beds thus designated appear to represent beds generally considered transition beds between the Cleveland and Chagrin by the writer and others. The need or desirability of introducing a new name for transition beds at this horizon is a question on which, doubtless, different views will be held. Arguments could be offered for a new member at the top of the Cleveland where locally there is some interbedding. The writer, however, doubts the desirability of introducing a new term for either set of beds. Professor Cushing believes this Olmsted formation to be unconformable with the Chagrin. Evidence will be offered on later pages indicating that sedimentation was interrupted at this horizon. Professor Cushing is in error in supposing that most of the collections of Cleveland shale fishes have come from his Olmsted shale. One of the richest localities known lies within the limits of the Cleveland and above the Olmsted as these are delimited on Professor Cushing's manuscript map. Nearly one-fourth ton of these fossils were taken last summer from this locality in the Cleveland. It is unfortunate that Professor Cushing should have interpreted the writer's reference to the collectors who secured much of the fish fossils described by Professor Newberry as applying to the geologists of the Second Geological Survey of Ohio. The three or four collectors alluded to in the lines from my paper quoted by Professor Cushing were, so far as I know, never officially connected with the Ohio Survey. For their splendid unselfish labors in helping to make known the wonderful fish fauna of the Ohio shale I have only the highest admiration. In the matter of discovering and extracting these difficult fossils they were probably much more expert than the members of the Second Ohio or any other geological survey. But this appreciation must not lead one to overlook the fact that the chief interest of these men lay in securing good specimens rather than in fixing the precise horizon from which they came. Professor Cushing refers to my earlier suggestion that the fish cited by Professor Newberry as evidence of the Carboniferous age of the Cleveland might, through some error, have been derived from a higher horizon, as we now know his "Waverly" fauna, which he supposed to be at the base of the Cleveland, to have been. Against this suggestion Cushing quotes Professor Newberry to the effect that the three genera

† The age of the Cleveland shale, this Journal, vol. xxxiii, pp. 581-584, 1912.

referred for a discussion of the taxonomic features of this nomenclature to the papers of Prof. C. S. Prosser* on the nomenclature of the Ohio geological formations. Two of these terranes, the Cleveland and Huron, are black shales, while the third is a light colored more or less sandy shale. Professor Newberry,† in the original account of the formations, here termed the Ohio shale group, recognized three distinct terranes which he called, respectively, the Huron shale, the Erie shale, and the Cleveland shale. At a later period, during his earlier work, he confused the two black shale members of the Ohio shale as exposed near Lake Erie and considered them the same formation. Later, however, he discovered and corrected‡ his mistake and correctly placed the "Erie," now called Chagrin, shale between the two. Mr. Ulrich has fallen into a similar error chiefly through theoretical deductions, as already pointed out, in assuming that the Chagrin and the black shales represent distinct series of rocks. A somewhat detailed account of the relations of these three shales of the Ohio group to each other will, it is believed, be sufficient to correct this latest misconception concerning them.

A brief account of the essential characteristics of the three formations of the Ohio shale group as they are developed in their type sections, will be given before considering their characteristics and relations elsewhere. The Cleveland shale, which is the youngest member of the series, is represented in the vicinity of Cleveland by a fissile black bituminous shale which has a thickness ranging from about 35 feet in the east-

Polyrhizodus, *Cladodus*, and *Orodus*, were found by him in the Cleveland at Bedford. This is valid evidence that the fossils in question came from what Professor Newberry considered the Cleveland. But concerning their evidence for the Carboniferous age of the Cleveland it must be noted that since Professor Newberry's time the range of one of these genera, *Cladodus*, has been extended to the Middle Devonian (Eastman, Jour. Geology, vol. viii, p. 35). Its occurrence in the Cleveland, therefore, is without special significance as regards the age of the Cleveland. The two genera, *Polyrhizodus* and *Orodus*, are in the Newberry collection of the American Museum of Natural History. The Acting Curator, Dr. L. Hussakof, writes me that there is some doubt as to whether the specimen referred to the former genus really belongs to *Polyrhizodus*. The genus *Orodus* is represented by 21 recorded species from the lower part of the Carboniferous in the United States. With this extensive representation in the early Carboniferous it would be strange indeed if no Devonian forerunners had ever been found. The representatives of this genus reported by Professor Newberry in the Cleveland probably represent the Devonian heralds of the Carboniferous host which followed. The principal stratigraphic points raised by Professor Cushing have been fully discussed in the body of this paper.

*The nomenclature of the Ohio geological formations: Jour. Geology, vol. xi, pp. 533-537, 1903.

Revised nomenclature of the Ohio geological formations: Geol. Survey Ohio, Bull. No. 7, pp. 1-36, 1905.

†Geol. Survey of Ohio, pt. 1, Rept. of Progress in 1869, 1870, pp. 18-21.

‡Mon. U. S. Geol. Surv., xvi, p. 127, 1889.

ern part of the city to more than 60 feet on the southwestern side of Cleveland. It lies between the sandy gray shales of the Chagrin below and the gray or reddish Bedford shale above. About 75 feet of the gray Chagrin shale is exposed in Rocky River just west of Cleveland between the base of the Cleveland and lake level. The present name of these gray sandy shales which are basal to the Cleveland shale in the type area of the Cleveland is derived from the Chagrin River, which is located about 8 miles east of the City of Cleveland. The name was substituted for Newberry's term Erie shale by Prosser* because the latter name was preoccupied. The type section is thus described by Prosser:

"The name *Chagrin formation* is, therefore, proposed for this mass of argillaceous and arenaceous shales and calcareous layers on account of the excellent exposures on the banks of this river extending from Willoughby to the south of Pleasant valley. With perhaps the exception of the cliffs on the shore of Lake Erie, there are probably no finer outcrops of the formation to be found than those forming the steep banks of the Chagrin River. One and one-half miles south of Willoughby is a cliff nearly a hundred feet high and a magnificent one more than a hundred feet occurs a mile below Pleasant valley, about four miles up the river southeast of Willoughby."

The Huron or basal shale of the group was so named by Newberry because of the excellent exposures along the Huron River about 40 miles west of Cleveland. As originally defined by Newberry, the Huron shale is "a belt from ten to twenty miles in width, reaching from the Lake shore (Erie) at the mouth of the Huron River, almost directly south to the mouth of the Scioto."† This definition of the Huron by Professor Newberry appears to be hardly explicit enough for present-day work because it fails to exclude definitely the uppermost beds or Cleveland shale. Evidently if these two formations of the shale group have any distinctive physical characteristics they should be added to the original definitions of the Cleveland and Huron shales. The writer's studies in northern Ohio have shown that the two black shales of the Ohio group have certain distinctive physical characteristics.

Detailed study of a large number of sections from Lake Erie to Kentucky has shown that certain lithologic features characterize the upper and lower portions of the Ohio shale group and afford very important aid in identifying them. It has been found in studying a considerable number of sections that the lower part of the black shales above the Olentangy

* Jour. Geology, vol. xi, pp. 533-534, 1903.

† Geol. Survey Ohio, Rept. Progress in 1869, pt. 1, p. 18.

shale is everywhere characterized in Ohio by spherical concretions often of large size. Concretions of this type are entirely unknown in the Cleveland shale both in its typical area and outside of it. On the other hand, in the region where the Cleveland shale is typically developed the thin limy bands with cone-in-cone structure are common. This type of rock has never been found associated with the spherical concretions. As these two very peculiar and striking lithologic features characterize distinct parts of the Ohio shale group (upper and lower parts) from northern Ohio into Kentucky, they seem to be very valuable and desirable lithologic characters to use in discriminating the Huron from the Cleveland shale. Although careful watch was kept throughout the season, these two features were nowhere found in the same or even in closely associated beds. It is proposed, therefore, to limit the term Huron shale to those beds of the Ohio shale exposed on the Huron River, at Rye Beach and elsewhere, in which the spherical concretions occur and the Cleveland shale to the higher beds in which they do not occur and in which the cone-in-cone structure does occur. The spherical concretions are a persistent feature of the lower or Huron shale as far south as the first tier of counties in Kentucky.* The cone-in-cone bands of the Cleveland persist still farther and have been observed as far south as Irvine, Kentucky. Using these criteria for distinguishing between the two black shale members, the Huron will have in the Huron section a thickness of probably 100 feet. At the base of the Huron along the Olentangy River about 25 feet of gray argillaceous shales, known as the Olentangy, separate the Huron from the Delaware limestone.

If the convenience of those geologists who are engaged with the correlation and classification of rocks had been considered when our Paleozoic sedimentaries were laid down, we would no doubt have had the Ohio shale terranes definitely separated by diastrophic breaks and persistent in lithologic type.

* In the paper referred to (see p. 188), Mr. Ulrich has put the question whether the drill has ever been known to strike one of these concretions in the Huron east of Cleveland where he assumes its absence. The question of course assumes a negative answer and consequent confirmation of the claim of the proponder that both the concretions and the formation which they characterize are absent below the Chagrin. Let us put a similar question concerning the Cleveland. Has any one ever heard of a drill striking one of the flat fish-bearing, or one of the dike-like concretions, or a cone-in-cone band in the black shale under the Bedford southwest of Cleveland? In this region the curious wall-like concretionary structures are not uncommon and the flat concretions are abundant while the cone-in-cone bands are practically universal. The writer must confess that he has not heard of drillers striking any of these unique structures in either case. But this does not lead him to doubt either that the black shale below the Bedford to the southwest of Cuyahoga River is the Cleveland nor that the black shale below the Chagrin east of Cleveland is the Huron.

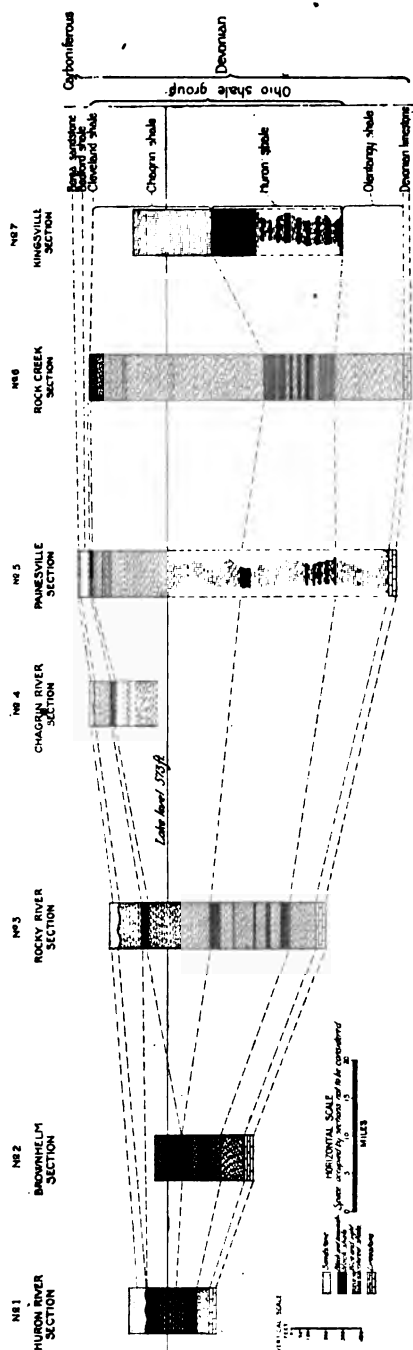


FIG. 2. Chart of sections* across northern Ohio from the Huron River to a point 10 miles west of the Pennsylvania line* along the line A-B, fig. 1.

* Section 1. represents a connected section based upon outcrops south and southeast of Sandusky in the Huron River valley and at the quarry 1 1/2 miles northeast of East Norwalk. The total thickness is checked by well records at Berlin Heights. Section 2. Authority, Edward Orton; Rept. Geol. Surv. Ohio, vol. vi, p. 487, 1888.

Section 3. This section is based upon the writer's notes combined with the record of the J. H. Wade well; Rept. Geol. Surv. Ohio, vol. vi, p. 429, 1888.

Section 4. Based upon the writer's notes.

Section 5. Based upon the author's notes and record of well 6 miles southwest of Painesville, located 1 mile west of Little Mt.

Section 6. Based upon author's notes on Trumbull Creek section and the record of the Rockville well, Rept. Geol. Surv. Ohio, vol. vi, p. 426, 1888. Depth of limestone in this well is assumed to be the same as in the Jefferson well 6 miles north-east; Bull. Geol. Surv. Ohio, 4th ser., No. 1, 1903, p. 303.

Section 7. Authority, record of the Jacob Flickinger well, Rept. Geol. Surv. Ohio, vol. vi, p. 423, 1888.

Unfortunately, however, the convenience of the geologist seems not to have been a factor in the agencies of sedimentation and we find an arrangement of unlike and intergrading sediments not easy to describe accurately and consistently in any scheme of taxonomic nomenclature. East of Cleveland the Ohio group includes three formations (see chart of sections, fig. 2), a black shale with interbedded gray shale at the base, followed by gray arenaceous shale with much interbedded sandstone in the upper part, which is terminated above by a second black shale. In going westward both the thickness of the Chagrin and the amount of sandstone in it diminish. In the Huron River section the moderately coarse sandstones of the Chagrin have disappeared altogether. While bands of blue argillaceous shale interbedded with black shale are conspicuous in the middle portion of the Huron River section, it appears impossible to distinguish the exact limits in this section of the portion equivalent to the Chagrin of the more easterly sections. Although the Chagrin epoch of sedimentation is believed to be as fully represented there as in the Cleveland section, it appears better from the taxonomic viewpoint not to attempt to apply the term Chagrin to any part of the Huron River section but to assign the whole of it to the two divisions which are pre-eminently black shales as proposed on an earlier page. The middle portion of the Ohio shale group as exposed along the Huron River is probably one-third or one-fourth blue shale. A representative example of this part of the shale is shown in the following section of the exposures near the bridge 3 miles southwest of Milan :

	Feet
Fissile black shale	12
Blue clay shale and some interbedded fissile black shale	20
Black shale	3
Interbedded blue gray clay shale and fissile black shale	4
Black shale with numerous spherical concretions.....	10

The two elements, blue and black shales, of such sections as this are not persistent for considerable distances if we may judge from the high variability of their thicknesses in the following section, which represents a horizontal exposure of about 250 yards immediately above the bridge at Milan, Ohio :

	Feet	Inches
Blue clay shale with 1-2 bands of black shale in middle. Large irregular-shaped concretions abundant in thicker part.....	1-4	
Fissile black shale with numerous large spherical concretions.....	9	
Blue clay shale.....		6-18
Fissile black shale.....	4-6	

Such variation in the thicknesses of the blue shale beds as those indicated above show that they pass laterally into black shales when followed some distance and *vice versa*. Prof. H. P. Cushing has called attention to a considerable mass of interbedded bluish gray and black shale at the base of the Cleveland shale, which he finds west but not east of Cleveland, named by him the Olmsted.* If, as the evidence appears to indicate, the Chagrin west of Cleveland grades into and becomes interbedded with the black Cleveland shale, just such beds as Professor Cushing has described would result from and represent this grading. Beds similar to Cushing's Olmsted also probably appear in the same general region near the Huron-Chagrin contact, and the gradual relative thickening westward of both basal and terminal zones of these gradational transition beds results in a series of interbedded blue and black shales in the Huron River section in which it seems to be impracticable to discriminate the precise limits of the Chagrin. The essential fact or feature involved in the preceding discussion of the sediments of the Ohio group is the marked lithologic differences between eastern and western sections and the decrease in coarseness of the Chagrin sediments from east to west or in a direction away from their source.

This fact of the lithologic change in the character of sediments between eastern and western sections is not provided for in Mr. Ulrich's doctrine of the persistence of lithologic units, and we find him using it as an argument against the continuity of the Chagrin into the Huron River section. Let us consider briefly whether the variation of the lithologic features of the Chagrin outlined above are consistent with the present operation of the agents engaged in distributing marine sediments. Under ordinary conditions the two agents engaged in this work are waves and currents. Very fine sediments are carried chiefly by currents which may carry them great distances regardless of depth. Coarse sediments are dependent for transportation chiefly upon wave action, which may remove them to any distance from the coast whence they were derived that prevailing winds and depth will permit. Depth is the sharply controlling factor in the operation of this agent. Wherever the water becomes too deep for waves to act effectively on the bottom, there coarse sediments will cease and fine ones begin. Corresponding changes in the character of the fauna may be expected along this border line as the joint result of change in depth and in the character of the bottom. The differences then between the lithology of the Chagrin in northeastern Ohio and its supposed equivalent in the Huron River section are only such as we should expect to find if the sea were materially

* This Journal, June, 1912, p. 583.

deeper in the latter than in the former region. If, as the evidence seems to indicate, the sea deepened rather rapidly west of Cleveland during the Ohio epoch, wave action would have become in that region powerless to remove coarse sediments beyond the latitude of Lorain. No one who is thoroughly familiar with the Devonian stratigraphy of New York and the northern Allegheny region would ever think of using difference in coarseness of materials, or difference in thickness of beds of supposed synchronous age, as an argument against their simultaneous origin in different areas of the same sea. Numerous examples of such changes could be given from this region, but one will suffice. The first Hamilton section west of Harrisburg shows nearly 800 feet of coarse sandstones with typical Hamilton shale and fossils above and below, the whole having a thickness of about 1000 feet. Eighty miles to the westward at Altoona the Hamilton formation is 500 feet thick, composed of dark olive-gray shales without a trace of sandstone in it.

The relations of the different types of sediments in the Ohio shale group are graphically shown in the accompanying east-west cross section figure 3. The observations of the writer all indicate conformable relations between the different shales of the Ohio group and between the base of the latter and the Olenotangy. The positive evidence which can be adduced for the conformable relations of these beds includes interbedding and intergrading of the Cleveland and Chagrin types of sediments. We may here profitably use Mr. Ulrich's testimony as to the validity of this class of evidence for conformable relations. Mr. Ulrich has, in his paper (see p. 188) referred to the writer's earlier allusion* to the unconformity at the top of the Chattanooga shale in Tennessee. He quotes from the folio as evidence of local conformity at this horizon, that locally "the black shale seems to pass very gradually into overlying green shale which constitutes the base of the full Tullahoma section." Mr. Ulrich's claim, then, is that whatever the columnar section and the structure sections show, and whatever the text may say about these graphic representations of the Tullahoma-Chattanooga unconformity, the above reference to intergrading sediments is nevertheless sufficient evidence of conformable relations where they exist. Now the present interest in Mr. Ulrich's insistence upon intergrading of formations as evidence of conformability

* This Journal, vol. xxxiii, p. 121.

† Mr. Ulrich has also stated that the authors of the Columbia folio did not attach high importance to the Chattanooga-Tullahoma unconformity. It must be observed, however, that they made it the boundary between the Devonian and Carboniferous systems. Just how they could have given it more importance is not easy to see.

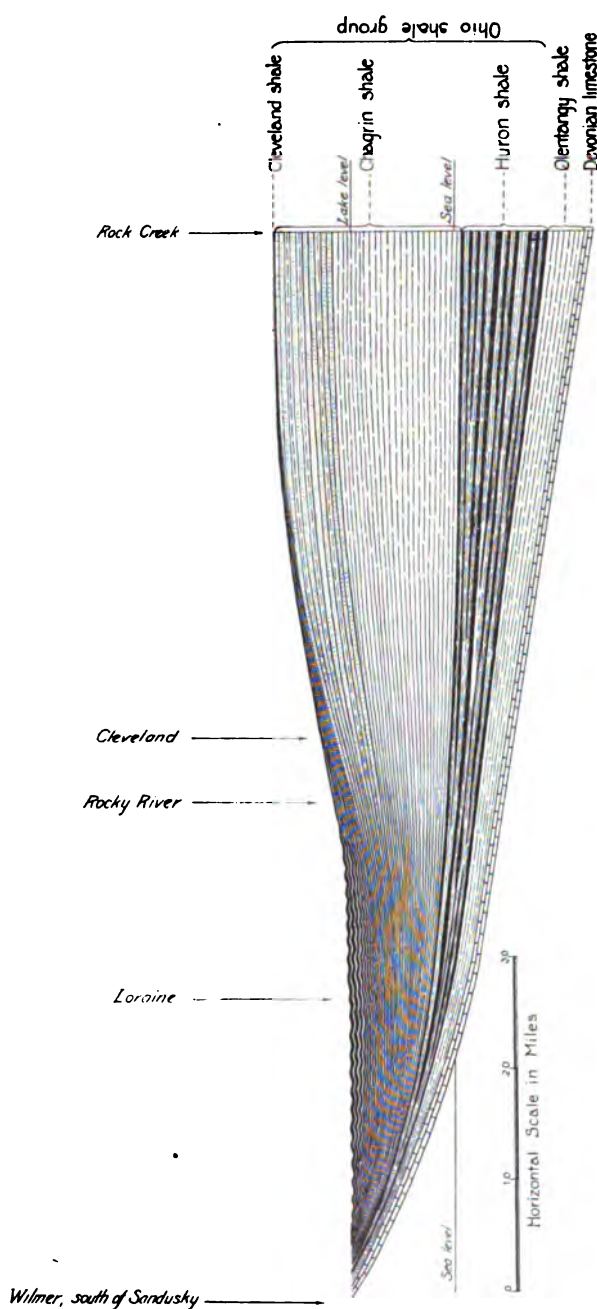


FIG. 3. Diagrammatic cross-section of the Ohio shale group and underlying beds from Sandusky along the Lake shore to Rocky River, thence to Rock Creek, Ashtabula County, Ohio. The section illustrates the thinning of the Ohio shale group from east to west and the lateral grading of gray into black shales. The abrupt change from the uniform westerly dip of the Cleveland shale to a series of low broad rolls is also shown. Vertical scale, 1 inch = 500 feet.

lies in the fact that there exists between the Cleveland and Chagrin shales just this kind of evidence of unconformity. If it is valid in Tennessee it must be in Ohio. A good illustration of this occurs in the Rocky River section one-half mile north-west of Kamms. Here the Cleveland shale type of sediment first appears as occasional one-inch bands interbedded with gray sandy Chagrin shale 20 feet or more below the base of the Cleveland or below where gray shales cease to appear. We find the same interbedding or intergrading at the base of the Huron which Ulrich has assumed to rest unconformably on the Olentangy. In the Deep Run section west of Lewis Centre three or four thin bands of fissile black shale appear interbedded with the upper part of the bluish gray Olentangy shale before it passes finally into the black fissile shale of the Huron.

The lithology of the black shale bears every evidence of being a deposit which formed at a considerable distance from a shore line. Not a trace of coarse sand, pebbles, or any kind of large rock fragments has been found in or at the base of these extremely fine-textured shales. This fact is entirely incompatible with the overlap hypothesis of the origin of these shales. The Chagrin shale, across which this hypothesis assumes the Cleveland shale sea to have advanced, comprises in its upper portion 100 feet or more of shales interbedded with thin bands of hard sandstone generally ranging from 6 inches to 2 feet in thickness. These sandstone bands comprise in many sections not less than one-fifth of the total mass of the Chagrin beds, and many of them are extremely hard and resisting. Wave action along the coast of a sea advancing across a wide tract of interbedded hard sandstones and unresisting shales such as these could not have failed to produce immense quantities of coarse shingle which would have been built into the beds of the overlapping sea and have left no question whatever of the actuality of the invading coast line. It is not on inference alone that this statement rests. The products of wave action now in progress upon a retreating coast line composed of Chagrin shale may be seen along the Lake Erie shore west of Rocky River, where immense quantities of pebbles, both large and small, have been made from the sandstone bands of the Chagrin shale. With this demonstration of what wave action actually produces in the shape of coarse materials when working on the Chagrin shale, the case of the overlap theorist falls to the ground unless he can show a basal conglomerate such as must have resulted from the advance of the sea across these beds. The work of various geologists on the northern Ohio section makes it very certain that there are no such beds. We can, therefore, only conclude that the assumed overlap never occurred.

Structural Features.—The Devonian limestone forms the floor of the Devonian shales everywhere in Ohio to the east of a line running from Columbus to Sandusky. The most important factor bearing on the areal distribution of these shales is a northern axis or branch of the great Cincinnati geanticline which runs north past Dayton between Toledo and Sandusky and pitches northward on reaching Lake Erie. Away from this axis the Devonian limestones dip to the eastward and southeastward. So far as drill records afford data this declination is always easterly but at a somewhat variable rate, ranging throughout eastern Ohio between 15 and 40 feet per mile. This easterly declination of the Devonian limestone appears to be a joint product of the Cincinnati uplift and the great downwarp trough in which the sediments comprising the western part of the Allegheny Mountains were deposited. Near Pittsburg the drill has shown that the Devonian limestone lies more than 5000 feet below sea-level. The great thickness of the Devonian and Carboniferous shale and sandstone series in eastern Ohio doubtless has a direct casual relation to the depth of this limestone floor. Its depression was doubtless in progress during much of this cycle of deposition, which in parts of western Pennsylvania dumped a thickness of more than one mile of sediments upon the sea floor during middle and late Devonian time. Owing to the great thickness of the Devonian shales in western Pennsylvania and eastern Ohio as compared with their slight thickness farther west, the inclination of the upper beds of this series cannot be expected to coincide with that of the limestone floor. If we take the thickness of the Chagrin and its underlying shales near the northeastern border of Ohio in Ashtabula County at 1800 feet, and at Cleveland 900 feet, which are close approximations to the actual thicknesses of these formations at these two localities, the top of the Chagrin and adjacent beds, if the formation were deposited on a horizontal sea floor, should dip to the west at 16 feet per mile owing to the excessive thickness of the beds at the east. Whether horizontal or inclined to the eastward, as at present, at the close of Chagrin deposition, the Devonian limestone, which is the basal formation of the Devonian shales, could not possibly have had the same declination as the upper surface of the Chagrin. It is the failure of Mr. Ulrich to recognize this fact that has led him to use different declinations of the shale and limestone as an argument for distinct marine basins for the Chagrin and the Cleveland. It is a simple mechanical fact due solely to differences in thickness of the Devonian shales at the eastern and western ends of the northern Ohio section, and has no bearing on the question of distinct marine basins of sedimentation for the different members of the Ohio shale. The gen-

eral relations of the Cleveland shale and the Devonian limestone across northern Ohio as regards dip are clearly shown in the chart of sections, figure 2. The well records show an eastward declination of the Devonian limestone across the northern part of the state which varies somewhat in different areas just as the dip of the outcropping Devonian shales, but conversely. Thus the easterly dip of the Devonian limestone from Wilmer, near Sandusky, to the Gillman well, $1\frac{1}{2}$ miles southeast of Huron, is 31 feet per mile; from the latter point to Lorain it is about 20 feet per mile. Between Lorain and Cleveland the rate decreases to about 10 feet per mile. From Cleveland to Jefferson near the northeastern border of the state about the same rate of 10 feet per mile is maintained.

We have for the declination of the base of the Cleveland shale the more precise data derived from surface observation and aneroid measurements of extensive exposures. The most easterly outcrop of the Cleveland shale examined is 2 miles west of East Trumbull, or 20 miles west of the Ohio and Pennsylvania state boundary. Here the base of the formation lies at about 990 feet above sea-level.* West of this point 11 miles, near Big Creek, the base of the Cleveland lies at nearly the same level, thus showing no dip. From the Big Creek section westward, however, there is a very gentle westerly dip. At Gates Mill, 17 miles west of the Big Creek section, the Cleveland has dropped to 880 feet, a dip of about 6 feet per mile. From Gates Mill to Rocky River west of Cleveland, a distance of 22 miles, the formation descends 200 feet or 6 feet per mile. A slightly lower rate of 8 feet per mile is maintained west of Rocky River between Dover Bay and the mouth of Porter Creek. West of Rocky River nearly continuous cliffs along the lake front continue with very few and short breaks nearly to Rocky River and afford opportunities for observing structural features along more than 12 miles of lake front unequalled in northern Ohio. For the first three miles of these cliffs there is no deviation from a uniform westerly dip of about 8 feet to the mile, a rate very similar to that prevailing for 40 miles east of Rocky River. At Eagle Cliff, however, the perfectly uniform gentle westerly slant of the strata, so well shown between Dover Bay pier and the mouth of Porter Creek, changes to a succession of low north and south trending anticlinal rolls. With few exceptions these structures have very low arches, nearly flat on top, which rise above their troughs from 3 to 8 feet. The width of these gentle undulations usually ranges between 200 and 350 yards, giving an effect not unlike the billowy surface of a subsiding sea. An exception-

* The figures given here are aneroid measurements checked with the nearest bench marks.

ally high arch just west of Eagle Point and another at Beach Park rise 20 feet or more. Detailed study of this lake shore section has shown that the east and west limbs of the series of low anticlinal rolls which succeed each other for more than 8 miles are essentially equal, and that for this distance the base of the Cleveland shale shows no westerly declination between Eagle Cliff and Lake Breeze.

In the vicinity of Lorain and for several miles to the westward the shales are concealed along the lake by glacial deposits. The shale cliffs reappear again, however, near the mouth of Vermilion River. Here along the shore east of the river the broad, low anticlinal rolls, similar to those which have just been described, prevail. These are interrupted by a fault which brings the Berea sandstone down to lake level and beneath which it dips at 45° . One other locality is known at East Norwalk, at the Shed and Perry quarries, where deformation has resulted in strong dips. There the Berea sandstone dips on the limb of a synclinal trough at 37° toward the southeast. Such strongly developed folds are very exceptional, however, the normal structure west of Rocky River being the very low rolls already described. Between the Vermilion and Huron rivers few if any exposures of the shale occur. West of the Huron River about 2 miles, the lowest and most westerly beds of the Ohio shale which are exposed along the lake shore reach the surface. Here the typical Huron shale with numerous large spherical concretions borders the lake. Since the Huron shale east of this point is everywhere below lake level, there is between the Huron and Vermilion rivers evidently some easterly dip of the surface beds. The more essential facts developed in this study of the structure of the Lake Erie section of the Ohio shale may be briefly summed up thus: At the western end of the section the shales have their minimum thickness and for a short distance eastward their upper and lower beds maintain an approximately similar easterly dip corresponding to that of the limestone floor, which is between 30 and 35 feet per mile in the Huron River valley. With the thickening of the shale eastward the dip of the upper or Cleveland shale division exposed along the lake shore ceases to correspond to the lower beds of the shale, which must continue to approximate the easterly dip of the limestone base. These upper beds for a considerable distance east of the Vermilion and Black rivers are characterized by a series of minor very gentle north and south rolls, but their total declination east or west is approximately zero. This is the result apparently of the easterly thickening of the shales keeping pace with the declination of the limestone toward the east. Near Rocky River and thence eastward for about 40 miles beyond Cleve-

land the easterly thickening of the shale series proceeds at a more rapid rate than the easterly dip of the limestone, and a westerly declination of from 6 to 7 feet per mile results.

Age of the Huron shale.—In testing the overlap hypothesis we are concerned more directly with the age of the Huron or basal shale of the Ohio group than with the age of the Cleveland. For this reason, and because of the limitations of space the present discussion of faunal evidence is confined chiefly to the Huron. The upper Devonian age of the Chagrin shale is generally conceded, and more detailed consideration of its correlation is not essential to the present discussion.

It has been pointed out elsewhere in this paper that the black shales in the Huron River section known as the Huron and Cleveland, while synchronous in part with the Chagrin shale to the east, represent, in the writer's opinion, a distinct bathymetric facies from it. The latter represents the shallower inshore facies, and the former the deeper water and more pelagic facies of the same sea, just as the upper part of the Hamilton of eastern New York and the Genesee shale represent distinct bathymetric conditions and equally unlike faunas. For this reason there is but little in common between the faunas of the dark colored members of the Ohio and the light colored Chagrin. The paleontologic evidence of the age of the Huron is of prime interest in this connection because of its bearing on the overlap theory. Since this hypothesis assumes the Carboniferous age of the Huron, the discovery in it of Carboniferous fossils is essential to its demonstration, or of Devonian fossils for its rejection. The report of David White on some well-preserved plant remains collected from beds within 10 feet of the lowest exposures of the Huron shale on the Huron River are of considerable interest in this connection. It is as follows:*

"I have examined with great care and interest the fossil plant from the Huron shale, near Milan in northern Ohio. The fossil comprises a long fragment of the trunk of the type described by Sir William Dawson as *Calamites inornatus*. On examination I find the species to present the essential characters of Nathorst's genus *Pseudobornia*, which is typical of the Pseudoborniales—an order that probably is ancestral to both the Sphenophyllales and Calamariales.

The specimens, as originally described by Dawson, are said to have been obtained from the Genesee shale along the shore of Cayuga Lake in New York. I have examined similar material collected by Prof. C. S. Prosser from the upper part of the Genesee shale at Blacksmith's Gully, near Bristol Center, Ontario County, New York, and from Seneca Point on the west shore

* Letter to the writer Dec. 18, 1911.

of Canandaigua Lake. It is represented in other collections by many specimens from the Genesee shale, from Mt. Morris, New York, and other localities. The form—probably identical with *Pseudobornia inornata*—is said to have been collected from shales referred to the Hamilton at Livonia, New York. Other material, probably belonging to the same genus but concerning whose specific identity there remains doubt on account of the lack of characteristics in ordinary stem fragments, is said to have come from the Marcellus at Collingwood, Canada, and 18-Mile Creek, in New York.

In its typical form the species is—so far as I am aware—characteristic of the Genesee shale.”

This plant is an abundant fossil in some parts of the Huron shale, although generally found in a fragmentary condition as though transported from a distance. It outnumbers all other fossil plants combined, if we except *Sporangites*, which are found in the Huron. The testimony of Mr. White that this dominant fossil plant is characteristic of the Genesee shale and is not known to occur above it should have much weight in establishing the Devonian age of the shale and the untenable position of the advocates of the overlap hypothesis.

The invertebrate fauna of the Huron shale, like that of most black shales, is very sparse indeed. Only one brachiopod with a general distribution has been observed. This is *Lingula ligea*, which has been found at Rye Beach and other localities where the lower beds of the Huron are exposed. This shell has a recorded range from Hamilton to Portage. The collections of the writer from the type region of the Huron shale include, in addition to *Lingulas*, a well-preserved *Paleoneilo*. This shell is closely allied to if not identical with the Hamilton species *Paleoneilo tenuistriata*. It was collected from a gray band within 5 feet of the base of the Huron as exposed on Huron River. Another molluscan form collected from the Huron at Rye Beach is a *Macrocheilus*. The surface features are not preserved but the shape of the mould indicates a species closely allied to if not identical with *Macrocheilus hamiltonæ*.

The Huron and Cleveland shales together afford a rather long list of fishes. But only a small number of these are known elsewhere. Concerning the evidence of this class of fossils it is sufficient to state here that Eastman, Hussakof, and Branson,* the three paleontologists who have in recent years given most attention to the Ohio group fishes, agree in considering these fossils to represent a Devonian horizon. Dr. Eastman† makes

* Notes on the Ohio shales and their faunas, University of Missouri, Bull. Science ser., vol. ii, pp. 23-32, pls. 1-3.

† Letter to the writer April 10, 1912.

the following statement regarding the affinities of the fish fauna:

"There are three genera of Genesee fishes which occur also in the Ohio shale, one of them represented by an identical species. These are: *Glyptaspis*, *Aspidichthys*, *Callognathus serratus*. These three are in addition to *Dinichthys*, already mentioned, making four in all, and I should not be surprised to find this number increased with later discoveries."

Conodonts are nearly everywhere common or abundant fossils in the Huron shale. But it is desirable to defer the discussion of their evidence until they have been more carefully studied.

The faunal evidence which has been presented represents a limited number of species, but it is uniform and consistent in indicating a Devonian horizon not later than Portage or Genesee. It is, on the other hand, irreconcilable with the overlap hypothesis. If, as the advocates of the Mississippian age of the Huron would perhaps claim, the Devonian species referred to above are recurrent forms which persisted beyond the limits of Devonian time, it is remarkable indeed that no Carboniferous fossils are associated with them to attest their transgression of the Devonian-Carboniferous boundary. The absence of such fossils renders such an explanation untenable. The rather close resemblance of the Huron and Cleveland shales in lithologic features is paralleled by faunal likenesses which are conspicuous in the conodonts and fishes. But there are also some faunal differences as well as likenesses. Some species have a restricted range comparable if not identical with the limited upward range of the large spherical concretions which characterize the Huron. *Dinichthys hertzeri* belongs with the group of species which do not range above the Huron shale. This species is known from the shore of Lake Erie at Rye Beach* to central Kentucky.† It has, however, never been found in the Cleveland shale although few if any fish-bearing horizons in the world have been more persistently searched by enthusiastic collectors than the Cleveland shale in the Cuyahoga and Black River sections. Professor Newberry's observation that the Cleveland shale fishes are in general of small size as compared with those of the Huron shale appears to be still valid. He wrote:

"In the Huron shale, on the contrary, we find the remains of fishes of enormous size, of most peculiar structure, and such as clearly belong to the Old Red Sandstone fauna so fully described by Hugh Miller.‡

* Branson, E. B.: Letter to the writer March 4, 1912.

† Kindle, E. M., this Journal, vol. xxxiii, p. 135, 1912.

‡ Newberry, J. S.: Report on the Geology of Erie County and the Islands, Ohio Geol. Survey, vol. ii, pt. 1, 1874, p. 188.

It is important to note, in seeking to determine the age of the Huron shale, that the shale immediately underlying it, the Olentangy of northern Ohio, is without question of Hamilton age.* Evidence has been offered elsewhere in this paper indicating the conformability of the Olentangy and the Huron. It is, therefore, not surprising to find, as has been pointed out, that the fossils of the Huron all find their equivalents or nearest allies in the fauna of the Hamilton or Genesee. This alignment of the Huron fauna affords unequivocal evidence against the assumption of its Carboniferous age involved in the overlap hypothesis, and consequently against this hypothesis itself.

Upper limit of the Devonian shales.—The diverse opinions which have prevailed on this question among geologists are well known. Professor Newberry, it will be remembered, even placed the Chemung of New York in the Carboniferous system. With his unique views regarding the place of the Chemung in the general time scale, it is not surprising that he should have at one time placed the Cleveland and "Erie" (Chagrin) shales of Ohio both in the Carboniferous.† In recent years geologists with few exceptions have discarded Newberry's classification and agreed in placing the Devonian-Carboniferous boundary above the Cleveland shale, either at the base or the top of the Bedford shale. The official reports of the Ohio Survey since 1887 have generally placed it at the base of the Bedford. Two recent papers‡ on northern Ohio geology have placed this boundary at the top of the Bedford shale. The faunal evidence for this assignment of the boundary has been fully presented in the paper by Dr. Girty, to which the reader is referred. There has recently become available through the work of Prosser,§ Burroughs,|| and Cushing¶ conclusive evidence of an important unconformity at the top of the Bedford shale which, in the judgment of the writer, strongly supports from the physical side the evidence from the biological side presented by Girty for placing the boundary between the Devonian and Carboniferous systems at the contact of the Bedford shale and the Berea sandstone. This is the only stratigraphic break which has been demonstrated to exist between

* Stauffer, C. R. : The Hamilton in Ohio, Jour. Geology, vol. xv, p. 596, 1907.

† Rep. Geol. Surv., Ohio, vol. iii, pt. 1, 1878, p. 18.

‡ Branson, E. B. : Notes on the Ohio shales and their faunas. Bull. University of Missouri, vol. ii, p. 28, 1912. Girty, G. H. : The geologic age of the Bedford shale of Ohio, Annals N. Y. Acad. Sci., vol. xxi, 1912. (In press.)

§ Prosser, C. S. : Manuscript, reference in Jour. Geology, vol. xix, p. 257, 1911.

|| Burroughs : The unconformity between the Bedford and Berea formations of northern Ohio, Jour. Geol., vol. xix, pp. 655, 659, 1911.

¶ Cushing, H. P. : Manuscript.

the base of the Olentangy and the top of the Bedford shale. Others have been assumed as corollaries of the overlap theory, but the mass of evidence already presented against this hypothesis removes them from consideration. The Devonian shales of Ohio represent a great series of alternating black and gray or bluish shale, in which the black color predominates to the westward and the gray color to the eastward. This succession of black, blue, and gray shale is broken for the first time by the appearance of red or chocolate-colored shale in the upper part of the Bedford. This earliest appearance in the Ohio section of red and chocolate-colored sediments in the Bedford shale indicates a change in the character and conditions of sedimentation of a more profound character than any which had previously occurred in the region since the cessation of limestone sedimentation. This type of sedimentation is terminated throughout northern Ohio by a very marked unconformity which intervenes between the Bedford shale and the Berea sandstone. The logical place at which to draw the Devonian-Carboniferous boundary in northern Ohio appears to the writer to be the horizon of this unconformity. The fauna of the Bedford shows a Devonian facies with the possible exception of *Syringothyris*, but this genus can no longer be regarded as strictly limited to the Carboniferous. The "Corry" sandstone of northwestern Pennsylvania, which follows the Bedford horizon and is the equivalent of the Berea, contains, according to Girty, a distinctly Carboniferous fauna. This definition of the boundary between the two systems gives as the initial formation of the Carboniferous a coarse sandstone holding an undoubted Carboniferous fauna which follows an unconformity above beds with a fauna which is more Devonian than Carboniferous in facies.

ART. XIX.—*The Estimation of Titanium in the Presence of Iron* ; by WILLIAM M. THORNTON, JR.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxiii.]

DURING the author's service as chemist on the Virginia Geological Survey a good many titaniferous rocks, containing the minerals rutile and ilmenite in various associations, were presented for analysis. Since the titanium content of these rocks was often high (amounting to 69 per cent in a few cases) it was necessary to resort to a reliable gravimetric method. Among the gravimetric methods in use at the present time that have been thoroughly tested, the one brought out by Gooch* is perhaps unequaled, and especially recommends itself because the iron can be completely separated from the titanium by a single treatment. This method provides not only for the separation of titanium from iron but also from aluminium and phosphoric acid. Since the Virginia rocks which ran highest in titanium were non-aluminous (or nearly so), it occurred to the author that the method might be so modified as to shorten the process and eliminate some of the more difficult manipulation.

The first step is to separate the iron. This is done by adding tartaric acid in quantity equal to three times the aggregate weight of the oxides to be held by it in solution. Hydrogen sulphide is then introduced until the iron has been reduced to the ferrous condition. Ammonium hydroxide is then added to slight alkalinity, and hydrogen sulphide again passed in until the iron has been completely precipitated and the solution left faintly alkaline to litmus paper. After filtration and washing of the ferrous sulphide with very dilute colorless ammonium sulphide, the titanium is entirely in the iron-free filtrate. The tartaric acid must next be destroyed; for titanium can not be precipitated by any reagent in its presence. This is done by acidifying the filtrate with considerable sulphuric acid, boiling out the hydrogen sulphide thus set free, and adding potassium permanganate (in the form of a strong solution) to the boiling solution until a permanent precipitate of manganic hydroxide appears, which is dissolved in a little sulphurous acid. The result of this reaction is that the tartaric acid is oxidized partly to formic acid and partly to carbonic acid. The titanium can then be precipitated by the basic acetate process. Much manganese is thus introduced into the solution and is co-precipitated in some measure with the titanium—necessitating a solution of the precipitate and a second precipitation of the titanium by the above mentioned

* Proc. Am. Acad. Arts and Sci., n. s., vol. xii, p. 435.

process. This makes no difference when the amount of aluminium is relatively large; for, although titanium can be completely thrown down in a solution containing up to 11 per cent of absolute acetic acid and thereby separated from most of the aluminium (not from all of it), at least a second precipitation is required.

It seemed probable to the author that some oxidizing agent could be found by means of which the tartaric acid could be broken down and at the same time introduce no substance that would contaminate the titanic acid; so that in cases where the aluminium was small in amount relative to the titanium one precipitation would suffice. After several unsuccessful experiments with different oxidizing agents, the plan of using a mixture of sulphuric acid and fuming nitric acid was tried with very gratifying results.

Two standard solutions containing titanic sulphate were employed in the following experiments. The first was prepared by fusing Merck's titanium dioxide with sodium pyrosulphate, extracting the melt with 10 per cent sulphuric acid, filtering, and making up to a definite volume. The second was prepared by treating twice crystallized potassium fluorotitanate with concentrated sulphuric acid—the sulphuric acid being kept at the fuming point for several hours, poured into cold water, and filtered. In either case the solution contained about 10 per cent of absolute sulphuric acid. Duplicate portions of 25^{cm}³ each were taken for standardization. Ammonium hydroxide was added until the solution was nearly neutral (the approach to neutrality being determined by the formation of a turbidity which disappeared but slowly after vigorous stirring). About 1^{cm}³ of a strong solution of ammonium bisulphite was added as a precaution to prevent the precipitation of any iron that might accidentally have found its way into the solution. Five 5^{cm}³ of glacial acetic acid and 15 grams of ammonium acetate were also added and the volume was made up to about 350^{cm}³. The solution was then brought rapidly to boiling and maintained in ebullition for about two minutes. The titanium came down in flocculent and readily filterable condition. The precipitate was washed first with water containing acetic acid and finally with pure water. Ignition in contact with the paper was performed in the usual manner, and finally the heat of a Meker burner was applied for 20 minutes. Duplicate determinations agreed to within 0.0001 gm.

The first series of experiments were carried out with a view to determining whether or not the titanium could be completely recovered after destruction of the tartaric acid in a solution containing the same constituents as the acidified and

boiled filtrate from the ferrous sulphide in an actual separation. Accordingly, to a 25^{cm} portion of the standard titanic sulphate solution exactly three times the weight of the titanium dioxide in tartaric acid was added, followed by ammonium hydroxide to alkalinity and then 10 to 12^{cm} of concentrated sulphuric acid. The solution was then evaporated down to incipient charring of the tartaric acid. The basin* was then covered with a watch glass and the heating continued till further charring and frothing had taken place as much as the capacity of the vessel would permit. After cooling a little, 5^{cm} of fuming nitric acid were added through the lip opening with a pipette. After the first violence of the reaction was over cautious heating was applied. A vigorous reaction took place accompanied by much effervescence and copious evolution of brown fumes. The organic matter gradually disappeared. The effervescence became steady, finally ceased and the sulphuric acid began to fume. A pale yellow syrupy liquid resulted. The liquid was poured into 100^{cm} of cold water, and after filtration the titanium precipitated exactly as described under standardization, Table I shows the results of five experiments carried out in the above manner.

TABLE I.
The Recovery of Titanium after Oxidation of Tartaric Acid
by Sulphuric Acid and Fuming Nitric Acid.

No.	Titanic sulphate = By standardization TiO ₂ cm ³ . grm.		Found TiO ₂ grm.	Error grm.	Alkali salt
1.	25	0.1012	0.1015	+0.0003	HNaSO ₄
2.	25	0.1012	0.1013	+0.0001	HNaSO ₄
3.	25	0.1256	0.1264	+0.0008	HKSO ₄
4.	25	0.1256	0.1256	0.0000	HKSO ₄
5.	25	0.1256	0.1259	+0.0003	HKSO ₄

A solution of ferric sulphate was prepared by dissolving ferric ammonium alum in water and adding a little sulphuric acid to prevent the formation of basic salt. The solution was standardized by potassium permanganate which had previously been standardized against sodium oxalate.

In the second series of experiments actual separations of titanium from iron were carried out in the manner detailed in the introduction. The filtrate from the ferrous sulphide was

* A 200^{cm} platinum basin of the Blair type was found to be the most satisfactory for the purpose.

acidified with 12^{cm³} to 15^{cm³} of concentrated sulphuric acid and after evaporation down to a small bulk was transferred to a 200^{cm³} deep form basin, evaporated further, and the tartaric acid destroyed by the method above given. Table II shows the results of seven experiments.

TABLE II.
The Separation of Titanium from Iron.

No.	Ferric ammonium sulphate = Fe ₂ O ₃		Titanic sulphate = By standardization TiO ₂		Found TiO ₂	Error	Alkali salt
	cm ³ .	gram.	cm ³ .	gram.	gram.	gram.	
1.	20	0.1430	25	0.1012	0.1018	+0.0006	NaHSO ₄
2.	20	0.1430	25	0.1012	0.1016	+0.0004	NaHSO ₄
3.	20	0.1430	25	0.1012	0.1015	+0.0003	NaHSO ₄
4.	20	0.1430	25	0.1012	0.1013	+0.0001	NaHSO ₄
5.	20	0.1430	25	0.1012	0.1012	0.0000	NaHSO ₄
6.	20	0.1430	25	0.1256	0.1258	+0.0002	KHSO ₄
7.	20	0.1430	25	0.1256	0.1259	+0.0003	KHSO ₄

A method has been satisfactorily worked out for the separation of titanium from iron and destruction of the tartaric acid, of such a nature as to introduce no foreign substance that will contaminate the titanium when subsequently thrown down. Except for the evaporation of the filtrate from the ferrous sulphide, the operations can be quickly performed. Evaporation, however, is an operation which does not demand the analyst's constant attention.

ART. XX.—*Pleistocene Plants from the Blue Ridge in Virginia*; by EDWARD W. BERRY (with figs. 1-5).

SEVERAL years ago I received from Mr. E. C. Harder, formerly of the U. S. Geological Survey, three or four small pieces of leaf-bearing laminated clay that he had collected in 1908 while making a study of the iron ores of the Appalachian region in Virginia, the occurrence of which he mentioned in print in 1909.* About the same time I received from Dr. Thomas L. Watson, the State Geologist of Virginia, a second small collection from the same locality made by Prof. R. J. Holden of the Virginia Polytechnic Institute while engaged in a study of the iron ores for the Virginia Geological Survey. I am greatly indebted to all of these gentlemen for the opportunity of studying these fossils and for information regarding their occurrence.

While the species represented are few in number they are such a remarkable assemblage for such an inland and elevated locality, that they seem worthy of the following brief note.

The locality is on the western flank of the Blue Ridge near the town of Buena Vista in Rockbridge County, Virginia.†

The stratum containing the leaves outcrops somewhat north of the junction of Big and Little Chalk Mine runs in the westernmost open cut of the Buena Vista iron mine, which has gone out of working and at present is being worked for clay by the Dickenson Fire Brick Company. The leaf-bearing layers constitute a lens of silty gray or brown, thinly laminated clay of limited extent and with a maximum thickness of 20 to 30 feet and a dip of 20° to the east. This lens, according to Prof. Holden, is underlain by the residual materials of the much folded Cambrian shales (Buena Vista or Watauga shale) and overlain by drift material from the adjacent mountains. Immediately below the lens the material is a white clay and according to Mr. Harder its upper portion contains quartzitic boulders ("river jacks"), decomposed chert fragments, local pockets of lignite and thin layers and lenses of more sandy materials.

Combining the results of an examination of the two collections yields the following plants:

CONIFERALES

Pinus sp.

A single asymmetrical flat seed 2.5^{mm} wide and 3.75^{mm} long, with traces of a once present wing; very probably represents some species of *Pinus* at present specifically undeterminable.

* Harder, Bull. U. S. Geol. Surv., 380 E, p. 68, 1909.

† Lexington sheet of U. S. Geol. Surv.

Taxodium distichum (L.) Rich. Figs. 1, 2.

Holmes, Journ. Elisha Mitchell Soc., p. 92, 1885.

Hollick, Md. Geol. Surv., Pliocene and Pleistocene, pp. 218, 237, pl. 68, 1906.

Berry, *Torreya*, vol. vi, p. 89, 1906.

Journ. Geol., vol. xv, p. 339, 1907.

Amer. Nat., vol. xliii, pp. 432-434, f. 1, 2, 1909.

This Jour. (4), vol. xxix, p. 891, 1910.

Torreya, vol. x, p. 268, 1910.

Plant World, vol. xvi, pp. 39-45, f. 1, 2, 1911.

The deciduous twigs of the bald cypress, indistinguishable from the existing species, are very abundant in the deposits. This is an abundant species in the Pleistocene deposits of the Atlantic coastal plain and it has been recorded from a large number of localities distributed from New Jersey to Alabama. The fact that several of these localities are north of, or inland from, the present limits of distribution, together with abundant sub-fossil evidence of restriction of range, indicates that the species is slowly retreating southward as a result of gradual and but little understood climatic change. None of the known occurrences either recent or fossil are from an elevation as high as this or as far removed from the ocean except where the distribution has followed up river valleys like the Mississippi and Ohio rivers as far as southern Indiana. The Blue Ridge in central Virginia is about 150 miles in an air line from the Atlantic ocean, with an average elevation of perhaps 2,000 feet, while numerous knobs are considerably higher. The climatological station nearest Buena Vista is at Staunton about 35 miles to the northeast, where the elevation and topography are similar.* As regards temperatures the annual mean is 55° with absolute maximum of 103° and absolute minimum of -13° and mean maximum of 66° and mean minimum of 44°. The growing season extends from about April 15 to October 22 and the mean annual rainfall is 39.7 inches (spring mean 10.6, summer mean 11.6, fall mean 9.1, winter mean 8.4).

A rough estimate of the climatic requirements deduced from the present distribution of the bald cypress shows that the mean annual temperature of its habitat ranges from 55° in southern Delaware to between 65° and 70° in Georgia, Alabama, Louisiana and eastern Texas. The precipitation varies from 40 to 60 inches per annum and is between 45 and 55 inches over a large part of the area. Hence it may be inferred that optimum conditions for the Cypress are furnished by somewhat higher temperatures and more abundant rainfall than obtain at the present time in the Shenandoah valley. Other undoubted factors of importance are humidity and ground water level, data for which are not available. It seems evident, however, that present conditions in the Shenandoah

* U. S. Weather Bureau, Bull. Q, p. 255.



valley are unsuited for this species, which at best is of extremely slow growth and scanty reproduction. Since somewhat similar anomalies of distribution are illustrated by some of the fossil forms associated with the Cypress at Buena Vista, their general bearing will be discussed at the end of the enumeration of species.

FAGALES.

Quercus alba Linné

Mercer, Jour. Acad. Nat. Sci., Phila. (2), vol. xi, p. 281, 1899.

Penhallow, Trans. Roy. Soc. Can., vol. x, p. 74, 1904.

Amer. Nat., vol. xli, p. 448, 1907.

Berry, Journ. Geol., vol. xv, p. 342, 1907.

The white oak ranges from Maine to Florida and Texas and still grows in the Shenandoah Valley. Fossil remains have been recorded from the Interglacial deposits of the Don Valley, near Toronto, Canada, from the bone cave at Port Kennedy, Pa., and from the Talbot Pleistocene of North Carolina. A probably identical form which has been referred to *Quercus pseudo-alba* by Hollick* occurs in the Sunderland Pleistocene of Maryland, so that there is nothing remarkable in finding the white oak represented in the Pleistocene of Buena Vista.

Quercus predigitata Berry

Berry, Journ. Geol., vol. xv, p. 342, figs. 4, 5, 1907.

This species, the undoubted Pleistocene ancestor of the existing *Quercus digitata* (Marsh) Sudworth and *Quercus pagodaefolia* (Ell.) Ashe, was described from the Talbot Pleistocene of North Carolina. It is exceedingly abundant in the Pleistocene shales at Buena Vista. The modern Spanish oak, which is very like *Quercus predigitata*, ranges from New Jersey to Texas and is for the most part a coastal plain species. It is said to extend up the Potomac River as far as Seneca Creek and is recorded by the Maryland Botanical Survey from the lower slope of Sugar Loaf Mountain in the upper Midland district of Maryland. Prof. Sudworth informs me he has found it in Stewart County, Tenn., and Shafer has reported it from Allegheny County, Pa. (Ann. Carnegie Mus., v. 1, p. 101, 1904). Prof. Sudworth, who kindly called my attention to the latter reference, doubts the authenticity of this record, but in the light of the abundance of *Quercus predigitata* in the Shenandoah Valley during the Pleistocene, it is not improbable that scattered descendants of it are still to be found west of the Blue Ridge.

* Hollick, Md. Geol. Surv., Pliocene and Pleistocene, p. 227, pl. 70, f. 2; pl. 71, f. 1-6, 1906.

ROSALES.

Crataegus sp. Fig. 3.

The handsome little leaf shown in fig. 3 is unquestionably a *Crataegus* and it would be a pleasure to be able to identify it specifically, but this is impossible in the present stage of our knowledge of the excessively numerous recent species of this genus.

The fossil suggests *Crataegus cordata* (Mill.) Ait., which is found in woods and thickets along the mountains from Virginia to Georgia. It also resembles *Crataegus apiifolia* (Marsh) Michx. with its long and delicate petiole, but the latter species is usually more lobate, relatively broader and with serrate teeth. I have collected leaves of *Crataegus coccinea* Linné in the coastal plain of North Carolina that only differed from the fossil in a shorter and stouter petiole. It seems unlikely that *Crataegus* had commenced to mutate into the existing irreco-g-nizable complex as early as the Pleistocene and the present fossil occurrence may possibly represent the Pleistocene ancestor of numerous existing species.

SAPINDALES.

Acer sp.

A single leaf of a specifically indeterminable species of maple is present in the collection.

ERICALES.

Vaccinium arboreum Marsh.

Berry, *Torreyia*, vol. ix, p. 73, 1909.

This Journal (4), vol. xxix, p. 398, 1910.

This species has been found in the fossil state in the Talbot Pleistocene of North Carolina and at a slightly older level along the Alabama River in Alabama.

In the existing flora it is found from North Carolina to Kentucky and south to Florida and Texas. It may be recorded from Virginia, but I know of no records of such an occurrence, so that the fossil record is considerably to the northward of its present range in the east.

SUMMARY.

The foregoing notes show that at some time during the Pleistocene several forms flourished on the western flanks of the Blue Ridge many miles distant from their present limits of distribution. What particular stage of the Pleistocene is represented by the clay lens is uncertain—possibly the late Pleistocene if any reliance can be placed on the Talbot occurrences of *Taxodium distichum*, *Quercus alba*, *Quercus predigitata* and *Vaccinium arboreum*. Such correlation data are con-

fessedly of untested value, however, and too much reliance cannot be placed on them.

Prof. Holden has called my attention to a small lake known locally as the duck pond about a mile northeast of the fossil plant locality on Big Pond Ridge, which occupies a similar position with relation to the underlying Cambrian. As limestones are present in the Cambrian shales this pond may be a solution pond, and this suggests a similar character and origin for the Pleistocene leaf-bearing lens. The fact that these Pleistocene shales dip 20° indicates a late solution of underlying calcareous beds.

The attitude of the area relative to sea-level in the Pleistocene is unknown—doubtless this region shared more or less in the oscillations known to have occurred in the coastal plain, and it is possible that an area of depression, when the waters of the Atlantic advanced inland over the Virginia coastal plain and converted the country immediately east of the Fall line belt into a region of estuaries, may have been a factor in the spread of the coastal plain vegetation through the water gap of the James River into the Shenandoah Valley. The alternative view, equally speculative, is that these elements of the present coastal plain flora were normally present in the Great Valley at this early period. Of the two the former seems the most probable.

Regarding climatic factors that may be legitimately deduced from these fossil plants, it is obvious from their present distribution that the mean temperature was higher at Buena Vista at this stage of the Pleistocene than it is now. While temperature is less of a factor in the details of plant distribution than has been commonly supposed, as Livingstone and Shreve have recently pointed out (Johns Hopkins Univ. Circ., 1912, No. 2, p. 19), the grouping of these fossil species in the existing flora in somewhat warmer areas is evident, since the more important moisture conditions (rainfall, humidity, etc.) as well as edaphic factors are not the same for the cypress, Spanish oak and arboreal vaccinium. The presence of the cypress at Buena Vista probably indicates a Pleistocene cypress bay or pond.

At the same time there is every reason to believe that the rainfall and humidity were both greater than they are at the present time along the western flank of the Blue Ridge. The presence of these, in the main more southern, species would indicate that the time was a late Interglacial period, but we know too little of the relation of vegetation to the continental ice sheets to the northward to be able to draw any legitimate conclusions on this point, and the deposits may well be post-glacial since the evidence for a mild climate immediately following the Wisconsin ice sheet is becoming established on a firmer footing with each additional fragment of evidence.

Johns Hopkins University, Baltimore, Md.

SCIENTIFIC INTELLIGENCE.

I. GEOLOGY AND NATURAL HISTORY.

1. *The Age of the Plant-bearing Shales of the Richmond Coal Field*; by EDWARD W. BERRY (communicated).—In the introductory paragraph of a recent article* describing an interesting new calamite type, *Neocalamites Knowltoni*, from the Richmond coal field, I stated that the containing beds are of Rhætic age as determined by Fontaine,† and not Keuper as stated by Stur,‡ Ward,§ Zeiller,|| and others. This statement was uncritical since it was based upon an only tentative examination of the question and an acceptance of some misleading identifications of previous students of our Triassic floras.

Shortly after the appearance of the article in question Professor Zeiller wrote to me questioning this statement of age and calling attention to certain continental floras in France, Lorraine and Saxony, both undescribed and recently described, that show similarities with the flora of the Richmond coal field. Unfortunately the latter flora is greatly in need of a modern systematic revision and the rich flora of Lunz in Austria with which Stur compared it has never been described or illustrated. This is also true of the large collections of Keuper plants from Thale, Harz, brought together by the late Professor Richter of Quedlinburg and recently acquired by Professor Nathorst for the Royal Natural History Museum of Stockholm.

Upon the receipt of Professor Zeiller's letter, I communicated with Professor Nathorst, who has devoted so many years to the elucidation of Rhætic floras, since there is no comparative material in this country of either Rhætic or Keuper plant life. He has had the goodness to make comparisons between the flora described from the Richmond coal field and extensive undescribed collections from Lunz in Austria and Thale in Saxony, in his possession. His opinion is entirely in accord with that of Professor Zeiller and he confirms for the most part the comparisons with the undescribed Lunz flora made by Stur.

The opinion of the two foremost students of fossil floras, both especially familiar with the Rhætic flora, must be considered as settling the Keuper age of the Virginia Triassic plant-beds, since the evidence upon which this opinion is based seems ample and conclusive.

Whether or not the whole thickness of our so-called Newark system of the Atlantic border is to be referred to the Keuper cannot be conclusively demonstrated at the present time. In this

* Berry, Botanical Gazette, vol. liii, pp. 175-180, pl. 17, 1911.

† Fontaine, Mon. U. S. Geol. Surv., vol. vi, 1883.

‡ Stur, Verh. k. k. Geol. Reichs., vol. x, pp. 203-217, 1888.

§ Ward, Bull. Geol. Soc. Am., vol. iii, pp. 23-31, 1891.

|| Zeiller, Ann. Geol. Universel, vol. v, p. 1247, 1888; vol. viii, p. 888, 1891.

connection a recent study of the Newark fishes by Professor Eastman* is of interest since it tends to confirm the preceding statements. After an extended comparison between the Newark fish-fauna and that of the European older Mesozoic, he arrives at quite different results from those of the late Professor Newberry and other American students of the Newark fishes, and concludes that there is a considerable parallelism between the fish-fauna of the Newark and that found in the Perledo limestone of Lombardy, a unit of the Buchenstein beds of the Alpine Muschelkalk, placed at the base of the Ladinian or the summit of the Virgilorian by various students. There is also a considerable parallelism between the American fauna and those of the Besano and Raibl beds of the Alpine Keuper.

Johns Hopkins University, Baltimore, Md.

2. *Geological Survey of New Jersey*; HENRY B. KÜMMEL, State Geologist. Bulletin 6, Annual Administrative Report of the State Geologist for the year 1911, including a report on Shark River Inlet by C. C. VERMEULE. Trenton, 1912. Pp. 82; 5 illustrations.—The work of the New Jersey Survey for 1911 included, as in past years, a wide range of scientific and economic problems. In geology proper there is to be issued before the close of the year "The Flora of the Raritan Formation" by E. W. Berry, who finds that the Raritan clays contain remains of seventy-eight genera, only thirty-two of which are extinct. A report on "Fossil Fish Remains of Cretaceous, Eocene and Miocene" is promised for October. An interesting feature of the present report is the advance summary of the conclusions of Professor Johnson that contrary to the accepted belief "there has been no appreciable subsidence of this coast within the last few thousand years."

H. E. G.

3. *Topographic and Geologic Survey of Pennsylvania*; RICHARD R. HICE, State Geologist. Report No. 4, The Mineral Pigments of Pennsylvania, by BENJAMIN L. MILLER. Pp. 101; 21 plates, 9 figures.—About half of the natural mineral pigments produced in the United States is credited to Pennsylvania, and a report on this state is substantially a general report on the paint industry. Others receive the most attention; and the detailed description of individual properties includes a brief discussion of structure and stratigraphy. A chapter each is devoted to carbonate of iron paint ores, black shales, yellow shales, red shales, iron ores, and minor substances. Professor Miller's report will be found interesting in both its scientific and commercial aspects.

H. E. G.

4. *State Geological Survey of Wyoming*, Bulletin 2, Series B, Geology and Mineral Resources of a Portion of Fremont County, Wyoming; by C. E. JAMISON, State Geologist. Pp. 90; 14 plates, map in pocket.—Increased interest in the oil fields about Lander, Wyoming, justifies a study of this region supple-

* Eastman, Bulletin 18, Connecticut Geol. and Nat. Hist. Survey, 1911.

mentary to the report of Woodruff (U. S. Geol. Surv., Bulletin 452). Geographic and stratigraphic data have been given ample consideration (pp. 1-52).

H. E. G.

5. *Maryland Geological Survey*; WILLIAM BULLOCK CLARK, State Geologist. 1911.—This Journal has recently received the following publications of this Survey:

Prince George's County. Pp. 251; 12 plates, 3 figures, atlas in separate case accompanying report. This contains the following papers: Development of knowledge concerning the physical features of Prince George's County with bibliography; Physiography of Prince George's County; Geology of Prince George's County; Mineral Resources of Prince George's County; by Benjamin L. Miller. Also the following: Soils of Prince George's County, by J. A. Bonsteel; Climate of Prince George's County, by Wm. H. Alexander; Hydrography of Prince George's County, by F. H. Newell; Magnetic Declination in Prince George's County, by L. A. Bauer; Forests of Prince George's County, by F. W. Besley.

Volume IX of the general reports. Pp. 348; 26 plates, 8 figures. This contains: Third Report on State Highway Construction for period from January 1, 1908 to January 1, 1910, by W. W. Crosby; Summary Final Report on the work of the Highway Division of the Maryland Geological Survey, 1898-1910, by Wm. B. Clark; Fourth and Final Report on State Highway Construction, to June 1, 1910, by W. W. Crosby; Report on the Iron Ores of Maryland with an account of the Iron Industry, by Joseph T. Singewald, Jr.; Report on the lines of Equal Magnetic Declination in Maryland for 1910, by L. A. Bauer.

Report on the Cretaceous Geology and Paleontology of Maryland. Pp. 622; 97 plates, 15 figures. This contains the following: The Lower Cretaceous deposits of Maryland, by Wm. B. Clark, A. B. Bibbins, and Edw. W. Berry; Lower Cretaceous Floras of the World, by Edw. W. Berry; Correlation of the Potomac Formations, by Edw. W. Berry; Reptilia of the Arundel Formation, by Richard Swann Lull; Systematic Paleontology, Lower Cretaceous, by R. S. Lull, W. B. Clark, E. W. Berry.

H. E. G.

6. *Cape of Good Hope, Department of Mines, 15th Annual Report of the Geological Commission, 1910*; A. W. ROGERS, Director. Pp. 142, vi, maps and figures. Cape Town, 1911.—The report of the Cape of Good Hope Geological Commission for 1910, delayed in publication, reveals, as usual, a large amount of careful field and office work, both reconnaissance and detailed. The unsatisfactory features of the present report are inadequate maps and illustrations. Certainly for foreigners, and probably also for natives, the plan of publication adopted by the New Zealand Survey or the U. S. Geological Survey is much more satisfactory. The report contains the following papers: (1) Survey of parts of Beaufort West, Fraserburg, Victoria West, Sutherland, and Laingsburg, by the Director, A. W. Rogers, interesting

features of which are the description of "pans" in the dolerite area, vertebrate fossils in the Beaufort Series, and the extremely interesting Nieuweveld deposits (pp. 25-32) where coal occurs not as strata but after the manner of igneous dikes or quartz veins. Dolerite sheets and dikes, cut by dikes and pipes of mica peridotite, grorudites (?) (new to the Cape), saxonite, etc., are described petrographically.

(2) Survey of the Maclear and Portions of Engcabo, Mt. Fletcher, Qumbu and Mount Frere, by Alex. L. du Toit. An areal study of the Beaufort and Molteno formations, and especially of the Qubnexa coal and Cave sandstone, was made. This latter formation is intimately connected with volcanic activity, and replaced in some areas by 1000-1500 feet of ash.

(3) Survey of Copper-Nickel Deposits of Insizwa, Mount Ayliff, East Griqualand, by A. L. du Toit. This is a petrographic study of a group of intrusives ranging from gabbro and norite to picrite, which with their contact phenomena have not been previously described. Copper and nickel of economic importance occur at the contact of the Insizwa intrusions and the Beaufort Beds.

H. E. G.

7. *A Monograph of the British Desmidiaceæ*; by W. WEST and G. S. WEST. Vol. IV, pp. xiv, 194; 33 colored plates. London, 1912 (printed for the Ray Society).—The scope and purpose of this valuable work are briefly outlined in a review of the first volume, which appeared in this Journal several years ago (see vol xviii, 473; also xxi, 477). In the present volume the treatment of the large genus *Cosmarium* is brought to a conclusion, 26 species being described. The genera *Xanthidium* with 15 species and *Arthrodesmus* with 13 species are then taken up, and the discussion of the genus *Staurostrum* is begun, 41 species being considered. Of the 95 species included in the volume, 47 are already known from the United States, so that the importance of the work from the standpoint of the American student may again be emphasized. All of the species are figured on the accompanying plates.

A. W. E.

8. *Elementary Plant Biology*; by J. E. PEABODY and A. E. HUNT. Pp. xvi, 207; 91 text figures. New York, 1912 (The Macmillan Company).—In the teaching of botany in the secondary schools there is a strong tendency to lay stress on the physiological aspect of the subject. This tendency is well exemplified by the present text-book. The laboratory exercises are so arranged that the functions of plants are well brought out, while the morphology of the plant organs receives relatively less attention. Various topics dealing with agriculture and other branches of applied botany are likewise taken up. The illustrations are largely selected from other works.

A. W. E.

9. *Illustrated Key to the wild and commonly cultivated Trees of the northeastern United States and adjacent parts of Canada, based primarily upon leaf characters*; by J. F. COLLINS and H. W. PRESTON. Pp. ix, 184; 279 text-figures. New York, 1912 (Henry Holt and Company).—This little volume is intended

to enable persons to become acquainted with the trees in their vicinity without presupposing an extensive knowledge of botany. The characters emphasized therefore are those derived from the leaves and bark rather than from the flowers and fruit. The text-figures include outline drawings of the leaves and half-tone representations of the bark.

A. W. E.

II. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Introduction to Analytic Mechanics*; by ALEXANDER ZIWET and PETER FIELD. University of Michigan. Pp. ix, 378; 96 figures. New York, 1912 (The Macmillan Company).—This volume is based to a large extent on Ziwet's Theoretical Mechanics, but the Applications to Engineering have been omitted and the analytical treatment has been broadened; consequently it will be a useful book for a student who is familiar with the foundations of mathematics and is well advanced in pure mathematics, but as a text-book for an elementary class it would present difficulties. The author obviously takes the German point of view with reference to the subject. While this is doubtless valuable from the theoretical side, the English point of view has been more fruitful in the applications to the numerical solution of problems. One must regard the book to considerable extent as an introduction to theoretical or abstract dynamics rather than the placing of physical problems on a dynamic basis. The real difficulties of the subject are the applications to physical problems, and it is this which should be faced in an elementary course. The greater part of the book is theory. There are not a large number of solved examples, and only a moderate number of exercises for the student to work out. The book is written with care, and while one may not agree with the author's point of view, his own views are logically and consistently carried out.

W. B.

OBITUARY.

PROFESSOR FERDINAND ZIRKEL, the veteran mineralogist and geologist of Leipzig, died on June 11 at the age of 74 years. His work on the microscopic characters of minerals and rocks, published in 1873, played an important part in the establishment of the new science of Petrography. His other works were numerous and include a volume describing the rocks collected by the Clarence King Geological Survey of the 40th Parallel, and several editions of Naumann's Mineralogy.

PROFESSOR EDUARD STRASSBURGER, the noted German botanist, died at Bonn on May 19 at the age of sixty-eight years.

Dr. WILLIAM MCMICHAEL WOODWORTH, the zoologist, of the Harvard Museum of Comparative Zoology, died recently at the age of forty-eight years.

M. LECOQ DE BOISBEAUDRAN, the eminent French chemist and discoverer of the new element gallium, died recently at the age of seventy-four years. He was a corresponding member of the French Academy in the section of Chemistry.

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THE
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ART. XXI.—*Ionization by Collision in Gases and Vapors*;
by W. R. BARSS.*

Introduction.

THE experiments described in this paper were undertaken with the object of extending the results which have already been obtained in connection with the ionization current which passes through a gas when the pressure is not too high. The theory of Ionization by Collision has been developed by Townsend† and verified for many gases at low pressures by various experimenters, mainly Townsend and the students associated with him. Bishop‡ has submitted this theory to a more rigid test by extending the observations to higher pressures and also to mixtures of gases, the properties of the constituent pure gases being known. He has shown that Townsend's theory holds over a range of pressures up to forty centimeters in air, carbon dioxide, hydrogen and various mixtures of these gases.

An ionization current through a gas may be considered as passing through three distinct stages as the electromotive force is increased. In the first stage Ohm's law is approximately obeyed, the current rising proportionately to the electromotive force applied. In the second stage the current remains practically constant with small, if any, variations for large additions to the electromotive force. In the third stage, the current rises rapidly when the electromotive force is increased by a small amount. Townsend has shown that when the applied electromotive force is sufficiently strong, an ion will acquire sufficient velocity to produce new ions by colliding with the neutral molecules of gas which may be in the path of the ion.

* Thesis presented to the Graduate School of Yale University, June, 1912, for the Degree of Doctor of Philosophy.

† The Theory of Ionization of Gases by Collision.

‡ Phys. Rev., vol. xxxiii, p. 325, 1911.

This effect is greatly increased by increasing the electromotive force and hence the abrupt rise in the third stage of the current is explained. Townsend has also shown that if the applied electromotive force is not too great, the negative ion alone is effective in producing new ions; but as the applied force is increased and the sparking potential is approached, the positive ions also acquire the property of producing others to an appreciable extent.

When the initial ionization consists of positive and negative ions uniformly generated in a gas between parallel-plate electrodes by the action of Röntgen rays, Townsend has derived the following formula:

$$C = C_0 \frac{e^{aL} - 1}{aL}$$

where C_0 is the constant current when no new ions are produced by collision (second stage), C the current corresponding to any field strength X after collision has begun (third stage), L the distance between the plates, e Napier's base, and a the number of ions produced by each negative ion by collisions with gaseous molecules in passing through a centimeter of the gas. C , C_0 and L may be determined experimentally, and therefore a may be calculated. The accuracy of this formula has been tested and it has been found that for a given field strength and a constant pressure, the value of C/C_0 varies with L , but that the values of a are independent of L within the limits of experimental error.

When the pressure is constant, a increases with the field strength and approaches a maximum value, which is reached when the field strength is great enough to produce a new pair of ions at each collision. If the pressure is reduced, the field strength being constant, a increases to a maximum and finally diminishes again. This agrees with the theory, for at a high pressure the free paths of the ions are very short and the ions do not acquire a sufficient velocity to ionize by collision. As the pressure is reduced the free paths are lengthened and the proportion of collisions resulting in new ions is increased. When the pressure is reduced beyond a certain critical point, the value of a diminishes, for then the number of molecules of gas becomes less and therefore the number of ions produced by collision becomes smaller in the same proportion.

Townsend has also shown that

$$a/p = f(X/p)$$

where p is the gaseous pressure and X the field strength; the function f depending upon the nature of the gas. Experiments verify this equation very accurately for all the gases that have been employed.

Townsend has also shown that if we have C_0 ions set free by the action of ultra-violet light at the negative plate of the two parallel plates between which the electric field is established, the number of ions C , which reach the positive plate, is given by the equation

$$C = C_0 e^{aL}$$

where L is the distance between plates, e Napier's base and a the collision constant as before.

Again experiments have shown that the values of a obtained with Röntgen rays as the ionizing agent, are the same as the values obtained with ultra-violet light, other conditions being equal. That is, the negative ions produced in gases by Röntgen rays follow the same changes in ionizing power as the negative ions set free from a metal plate by the action of ultra-violet light.

Object of the present experiment.

It was found convenient in this investigation to employ alpha radiation as the ionizing agent. Moreover, as no determinations have hitherto been made for the collision constants corresponding to ionization by alpha rays, it was of interest to ascertain whether these constants were in any way dependent upon the nature of the ionizing source.

In addition, few experiments have been performed to determine these constants in the case of vapors. The only case reported is that of water vapor by Townsend.* The vapors employed in this experiment were sulphur dioxide, ethyl alcohol, ether, methyl iodide and ethyl chloride. In the measurement of ionic mobilities,† the vapors have given evidence of a characteristic behavior; so that it did not seem unlikely that ionization currents in vapors would also present distinctive features.

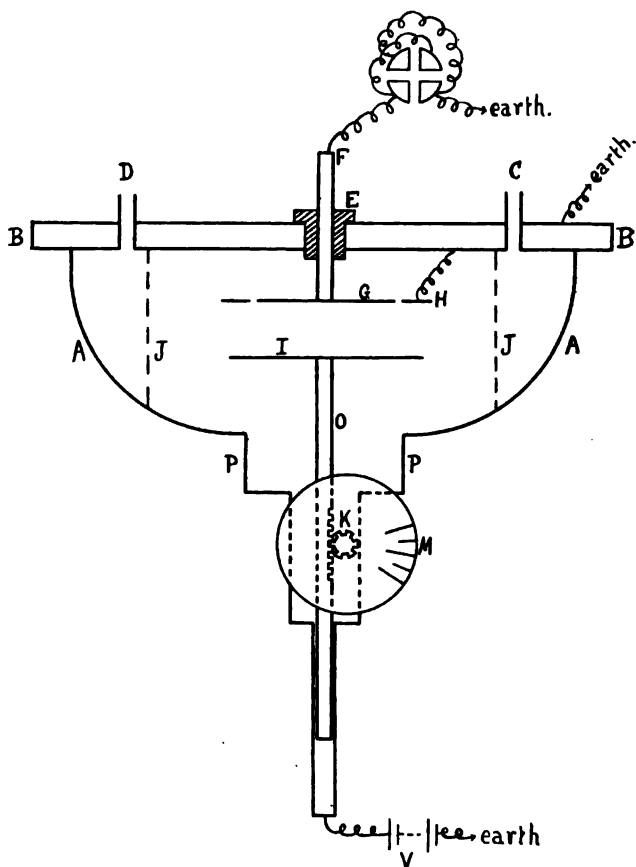
Apparatus and methods of experimenting.

The apparatus used in this investigation is shown in fig. 1. It consists essentially of two parallel plates inside an air-tight vessel. AA is a glass bell jar fitted with a brass cap PP and a separate brass top BB. Through an ebonite plug E, a brass rod F is passed by means of which the brass plate G is connected to one pair of quadrants of a Dolezalek electrometer, the second pair of quadrants and the case being earthed. The plate G is provided with an earthed guard ring H. A second plate I is connected by means of the brass rod O to a source of potential V. This plate I could be raised or lowered by means of the rack and pinion K, the distance between the plates being read by a graduated micrometer head M attached to the shaft

* Phil. Mag., vol. v, p. 389, 1903.

† Wellisch, Phil. Trans., vol. ccix, p. 249.

FIG. 1.



of the pinion. JJ is an earthed brass gauze to counteract any electrical effects from the surface of the glass jar. The opening D in the top BB was connected to a Töpler pump, an open manometer and a MacLeod gauge, so that all pressures up to an atmosphere could be measured. The opening C was connected to the vapor or gas supply. Connections from the chamber to the pump and to the gas supply were made of glass tubing. The joints between brass and glass were made airtight by sealing with rubber stopcock grease and soft wax. Connections from the chamber to the electrometer were provided with earthed guard tubes. A thin coating of powdered uranium oxide attached to the upper surface of the lower plate provided a suitable source of alpha radiation.

The experiments were conducted in the following manner: The rod connecting the plate G to the electrometer was earthed

through a potentiometer by means of a brass on brass contact key. The plate I being raised to the desired potential, the plate G was insulated and the deflection of the electrometer needle during a certain time was measured. By means of the potentiometer the volt sensitiveness of the electrometer at any time could be determined. Four or five trials were usually made for each observation, the separate trials seldom varying by more than three per cent from the mean.

Two preliminary experiments were made before the uranium oxide was put in the ionization chamber. The first was to test the electrical capacity of the apparatus (i. e., the parallel plate chamber and the electrometer system). To do this the lower plate was raised to a certain known potential which was kept constant. Electrometer deflections caused by the induced potential on the upper plate were measured for different distances between the plates. It was found that these deflections varied inversely as the distances involved, over the range of distances used in the later experiments (0.5cm to 2.5cm). This means that the capacity of the whole system is approximately constant. Since this is true, the ionization current will vary directly as the rate of electrometer deflection, so that the latter may be taken as a measure of the former.

The second preliminary experiment was to test for any ionization that might be due to the potential gradient between the plates. The vessel was evacuated to a pressure of one millimeter and the lower plate raised to high potentials. It was found that the electrometer showed no variation until the sparking potential was reached, for all distances down to 0.5cm between the plates; so that there was no ionization due to the electric field alone, before a discharge occurred.

EXPERIMENTAL RESULTS.

Gases.

The first experimental results were obtained in air at pressures of 4.17mm and 2.09mm . Three sets of readings were taken for each pressure corresponding to three different distances between the plates. Curves showing the relation between field strength (volts per centimeter) and ionization current are given in fig. 2 for a pressure of 4.17mm . Values of α were calculated from Townsend's formula, page 230, and are given in Tables I and II. The general shape of the curves as well as the values of α agree very well with Townsend's results. In Tables I and II, X is the field strength, L the distance between the plates. The figures in parentheses are taken from Townsend's results,*

* *Phil. Mag.*, vol. i, p. 208, 1901.

TABLE I.

Pressure, 4.17^{mm}.

X	α (L 2 ^{cm})	α (L 1 ^{cm})	α (L 0.5 ^{cm})
120	.13 (.13)		
160	.30 (.28)	.26 (.30)	
200	.50 (.50)	.48 (.51)	
240	1.08	1.14 (.99)	1.16
320		2.06 (2.1)	2.20 (2.2)
400			3.80 (3.6)

TABLE II.

Pressure, 2.09^{mm}.

X	α (L 2 ^{cm})	α (L 1 ^{cm})	α (L 0.5 ^{cm})
80	.15 (.13)		
120	.38 (.42)	.42 (.40)	
160	.87 (.90)	.89 (.90)	.92
240	1.63	1.61 (1.60)	1.55
320		2.50 (2.35)	2.52 (2.35)

for the same field strength, the same distances between the plates and pressures of 4.13^{mm} and 2.12^{mm}.

It will be noticed that the curve corresponding to a distance of 2 centimeters between the plates rises more abruptly than the curve corresponding to 1 centimeter; and in the curve corresponding to half a centimeter the current rises more slowly with the field strength than in either of the other cases. In other words, there is a divergence of the curves for different distances when the pressure is constant. When the plates are close together the mass of gas to be ionized is less, and we should expect, according to Townsend's theory, a smaller collision effect than when the plates are separated to a greater distance.

The next experimental results were obtained with hydrogen. The hydrogen employed was prepared by the chemical action of hydrochloric acid on zinc. It was then dried by being passed through tubes containing calcium chloride and phosphorous pentoxide, and further purified by the action of liquid air and charcoal. A series of curves was obtained at relatively high pressures (19.6^{cm}, 15.5^{cm}, 10^{cm}, and 4.2^{cm}), which agreed very well with those obtained by Bishop, who used ultra-violet light as the ionizing agent. The collision effect appears to set in at a smaller field strength; this probably points to the fact that in the present case a slightly higher degree of purity was obtained.

Curves were also obtained with different distances between the plates, the pressure being constant. The values of α calculated from these curves agreed very well among themselves, the greatest deviation being about 5 per cent.

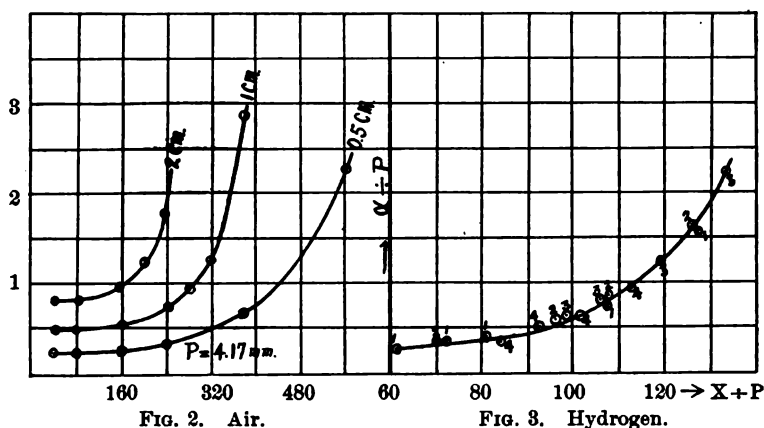
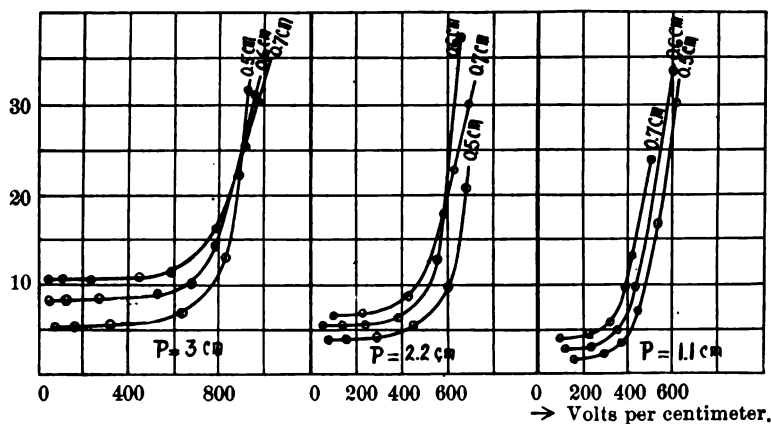
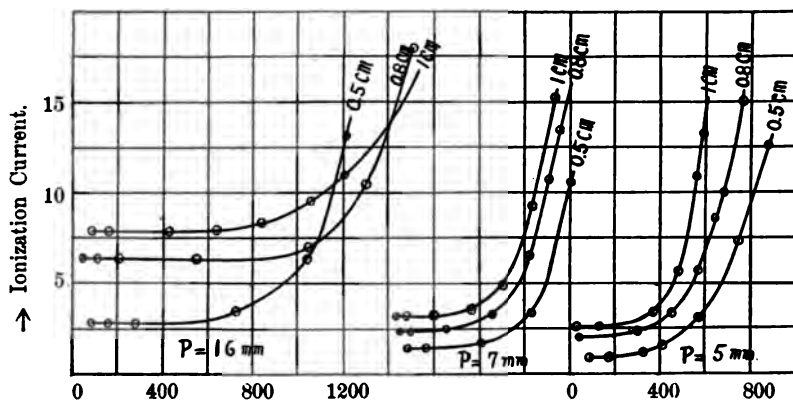


Fig. 3. Hydrogen.

0 400 800



As a further test the equation

$$\alpha/p = f(X/p)$$

was shown to hold. Since this equation is a general one, if we plot a curve for each pressure, taking as coordinates α/p and X/p , the curves for different pressures should coincide. This was tried for four different pressures in hydrogen. Values of α/p and X/p are given in Table III, and the curve connecting α/p and X/p is shown in fig. 3. Points on the curve marked

TABLE III.

1. $P = 15.5^{\text{cm}}$

X	α	α/p	X/p
960	0.80	0.05	61.9
1100	0.93	0.06	72.0
1260	1.08	0.07	81.3
1660	2.28	0.14	107.1
1980	4.88	0.31	127.7

2. $P = 10^{\text{cm}}$

X	α	α/p	X/p
700	0.60	0.06	70.0
960	1.08	0.10	96.2
1080	1.60	0.16	108.1
1260	3.28	0.32	126.0

3. $P = 4.2^{\text{cm}}$

X	α	α/p	X/p
400	0.46	0.11	98.0
450	0.63	0.15	107.4
500	1.0	0.24	119.1
580	2.0	0.47	138.2

4. $P = 19.6^{\text{cm}}$

X	α	α/p	X/p
1660	1.37	0.07	84.7
1800	1.76	0.09	92.0
1980	2.30	0.12	101.0
2240	3.81	0.19	114.1

1, 2, 3, and 4 correspond to pressures of 15.5^{cm} , 10^{cm} , 4.2^{cm} , and 19.6^{cm} respectively. It will be noticed that all the points calculated are close to a common curve, which agrees with the theory.

From these results in air and hydrogen, we may conclude that the negative ions generated in a gas by collisions with alpha particles are identical with those generated by Röntgen rays and ultra-violet light. In other words, the collision constants are independent of the nature of the ionizing agent.

Vapors.

The method of experimenting was the same for all vapors employed. The apparatus was evacuated to a low pressure (0.01^{mm}) and vapor was admitted to a pressure depending on the

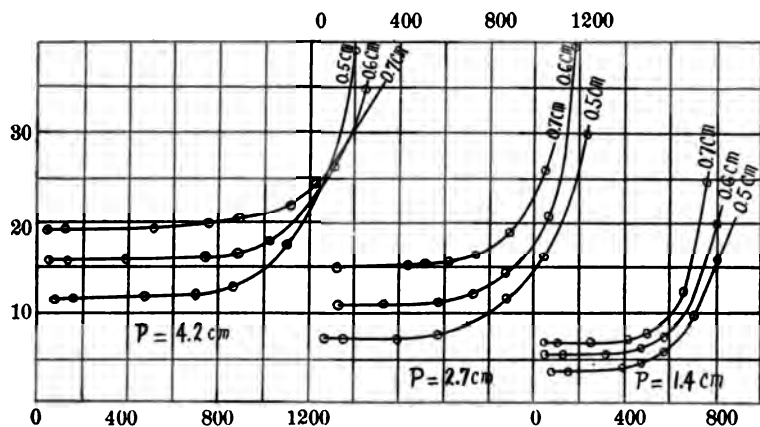


FIG. 6. Ethyl chloride.

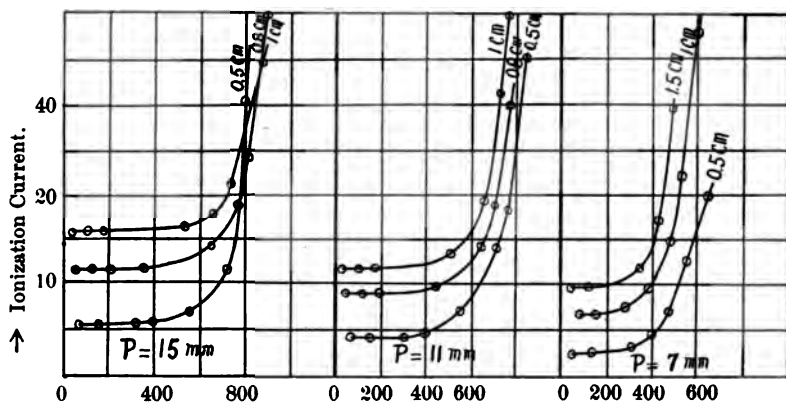


FIG. 7. Ether.

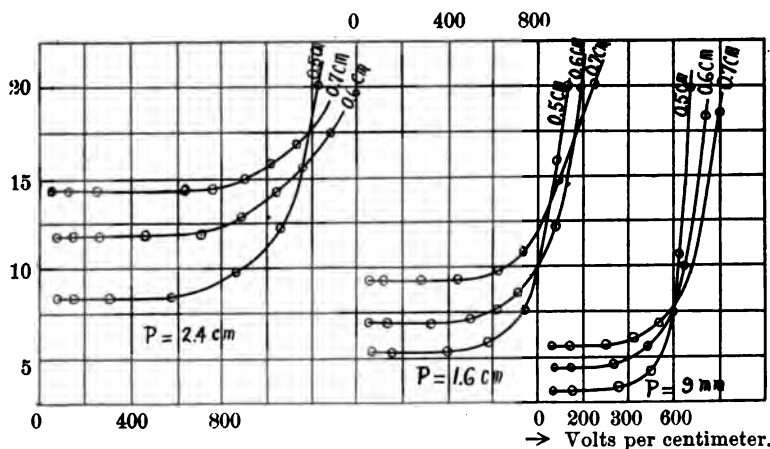


FIG. 8. Methyl iodide.

→ Volts per centimeter.

vapor pressure of the particular substance being used. This pressure was reduced by means of a water pump and the vessel was refilled with vapor. This process was repeated several times so that when readings were made a very small percentage of air was present with the vapor. Three sets of curves were obtained in each vapor corresponding to three different pressures, each set containing three curves corresponding to three different distances between the plates. These curves are shown in figs. 4 to 8 inclusive. In the vapor curves as in the air curves, ordinates represent ionization currents and abscissæ represent the field strength in volts per centimeter. In figs. 4, 6 and 8, the values of field strength for the middle set of curves are given at the top of the figures. A characteristic series of readings is given in Table IV. It was found that, for high pressures (9.9cm , 5.3cm and 2.9cm in SO_2), the ionization corresponding to saturating field strength was proportional to the pressure. This fact was observed for all vapors; and the result enabled smaller pressures, which could not be measured accurately by the open manometer, to be calculated.

The vapors were not admitted into the chamber at pressures high enough to produce any appreciable permanent condensation on the walls of the apparatus; for after each vapor was used, the ionization in air was tested, the results varying only as the sensitiveness of the electrometer varied. In every case there was no change in pressure during the time taken for a

TABLE IV.

SO_2 (pressure 1.6cm). See fig. 4.

X	δ ($L = 1\text{cm}$)	δ ($L = 0.8\text{cm}$)	δ ($L = 0.5\text{cm}$)
50		6.30	
80	7.98		2.85
100		6.30	
160	7.98		2.9
200		6.31	
280			2.9
420	8.03		
525			
780		6.30	3.35
795		6.41	
845	8.40		
1045	9.50		6.4
1056		7.15	
1200	11.10		13.0
1300		10.50	
1500		18.1	

series of observations, that could be detected by the manometer or the direct deflections of the electrometer.

In the above table, L is the distance between the plates and δ the corresponding electrometer deflection in centimeters per second.

Discussion of Curves.

The curves at the higher pressures in all the vapors employed give evidence of some extraordinary but characteristic behavior. The curve for a smaller distance between the plates rises more abruptly than that for a greater distance; so that the curves for two different distances cross each other. As the pressure is diminished, this process is somehow reversed, the curves becoming approximately parallel and finally diverging as the pressure becomes still further reduced. This is contrary to the behavior of gases in so far as we have experimental evidence, and is contrary to the facts that would be expected from Townsend's theory. According to this theory, for any pressure, provided it is kept constant, the curves corresponding to different distances between the plates should diverge, as they do at the lower pressure.

We have, therefore, experimental evidence which points to a distinct difference between gases and vapors, in so far as ionization by collision is concerned.

Values of a in sulphur dioxide at a pressure of 0.5^{cm} and in ether at a pressure of 0.6^{cm} (pressures at which the curves diverge) were calculated from the formula stated on page 230 and are given in Table V. The values of a for different distances between the plates agree sufficiently well to lead to the conclusion that Townsend's theory, as developed for gases, holds in vapors at low pressures.

TABLE V.

SO_2 , pressure 0.5^{cm} .

X	a ($L = 1^{\text{cm}}$)	a ($L = 0.8^{\text{cm}}$)	a ($L = 0.5^{\text{cm}}$)
280	0.17		
370	0.45	0.48	
500	1.75	1.75	1.90
580	3.41	3.25	3.44

Ether, pressure 0.6^{cm} .

X	a ($L = 1.5^{\text{cm}}$)	a ($L = 1^{\text{cm}}$)	a ($L = 0.5^{\text{cm}}$)
360	0.33	0.31	
530	1.75	2.02	1.8
610		4.13	4.3

The ionization in vapors was much more intense than in air under similar conditions of pressure, distance between plates and field strength. The thing which next suggested itself was to take air at a pressure that would give about the same ionization as that obtained with vapors (under saturating field strength) and to investigate for evidence of the crossing effect for different distances between the plates. Unfortunately when the experiment was tried, sufficient potential was not available to produce ionization by collision at the pressure required.

Reversing the electric field gave the same general results, the curves crossing for both positive and negative applied potentials.

Experiments with a Cylindrical Chamber.

It was thought that the apparent contradiction in the case of vapors might be due in some way to the collision effect of the positive ion; for, as stated in an earlier part of the paper, the ionic mobilities in vapors have given evidence of a characteristic behavior, that of the positive ion in some cases exceeding that of the negative ion.

To test for the relative ionizing powers of the positive and negative ions, a cylindrical ionization vessel was employed. A brass vessel 12.7^{cm} high and 6^{cm} in diameter was coated on the inside with powdered uranium oxide. A central brass electrode 0.3^{cm} in diameter, provided with an earthed guard ring, was connected to one pair of quadrants of the electrometer and an electromotive force was applied to the case of the chamber.

It has been shown that when the potential difference is small, the current through a gas in such a vessel is approximately the same whether the case has a positive or negative potential; but when the potential difference is large, the currents are no longer equal. When the case is negative, a large increase in current is obtained when the electromotive force is increased. In this case all the negative ions traverse the field of strong electric force near the central electrode, and consequently acquire a velocity sufficient to ionize by collision the molecules of the gas. When the case of the chamber is positive, the increase in current is relatively very small when similar increases in the electromotive force are made. This time the positive ions traverse the strong field near the central electrode and experiment has shown that they do not acquire sufficient velocity (no doubt due to their greater mass) to ionize by collision the molecules of the gas.

This effect was tried in air at a pressure of 3.8^{mm}, the resulting curves agreeing very well with those obtained by Kirkby.*

* Phil. Mag., vol. iii, p. 212, 1902.

Investigations were next made with sulphur dioxide and alcohol vapors for two different pressures in each. The results were of the same general nature as those obtained in air, thus showing that the positive ion in vapors plays a very small part in ionization by collision until the sparking potential is almost reached.

So far, the anomaly presented by the behavior of vapors has not been definitely explained. It may be due to some instability in the molecular structure of the vapors when they are acted upon by alpha radiation; in other words, the alpha radiation may be effective in producing a chemical change.

It is more probable that the anomaly may be explained by supposing the formation of aggregate molecules which act in the capacity of a thin metal wire in carrying a conduction current through the vapor. The continuity of these aggregate molecules would be more stable when the plates are closer together than when they are farther removed; and hence we would expect the current to increase as the distance between the plates becomes less. This fact experiment shows to be true. It is also possible that the formation of these aggregate molecules will be a function of the pressure, the number formed decreasing as the pressure becomes less until finally a pressure is reached when the current is not increased by this conduction effect, but is entirely due to ionization proper.

Summary.

The collision constants are shown to be independent of the nature of the ionizing agent; therefore the negative ions generated in a gas by collisions with alpha particles are identical with those generated by Röntgen rays and ultra-violet light.

The theory of ionization by collision as developed for gases holds for vapors ionized by alpha particles provided the pressure is not too great. As the pressure is increased, evidence of irregularity is obtained which seems to point to some instability in the molecular structure of vapors, either due to the formation of aggregate molecules or to some chemical change.

In vapors, as in gases, the negative ion alone is effective in producing new ions by collisions with neutral molecules, until the sparking potential is approached.

In concluding this paper, I wish to thank Professor E. M. Wellisch of the Sloane Laboratory for his many valuable suggestions and for his kindly interest throughout the experiment.

ART. XXII.—*Geology of Arisaig-Antigonish District, Nova Scotia* ;* by MERTON Y. WILLIAMS.

(Contributions from the Paleontological Laboratory, Peabody Museum, Yale University. — Abstract of a thesis presented to the Faculty of Yale University for the degree of Doctor of Philosophy, June, 1912.)

Purposes of the investigation and scope of the article.

DURING the summer of 1910 the writer and his assistant, Mr. M. H. McLeod of Northeast Margaree, Cape Breton Island, Nova Scotia, were engaged by the Geological Survey of Canada to make a detailed examination and survey of an area in northeastern Nova Scotia which it was hoped would furnish critical data for the unravelling of the Paleozoic stratigraphy of that part of the province. Pending the publication by the Geological Survey of the complete report with maps, the following summarized statement is offered as covering the most important conclusions.

Acknowledgments.

The writer wishes to acknowledge his indebtedness to Professor Charles Schuchert of Yale University and Professor W. H. Twenhofel of the University of Kansas for advice and assistance during the early part of the field work. Thanks are also due Professors L. V. Pirsson, Joseph Barrell, Isaiah Bowman, and J. D. Irving of the Geological Department of Yale University, for assistance in the preparation of the report here summarized.

Location and extent of the district.

The Arisaig-Antigonish district of northeastern Nova Scotia fronts on Northumberland Strait about one-third of the way from Cape George to Pictou Harbor. From a water-front 10 miles long with Arisaig Point at its center, the district extends inland 11 or 12 miles to the southeast, including the gypsum deposits south of the Intercolonial Railway. The approximate area studied is 115 square miles.

Previous work.

Geologically the region is classic as a result of the labors of Sir J. William Dawson† and the Rev. D. Honeyman‡ in

* Published by permission of the Director of the Geological Survey of Canada.

† Dawson, J. W., *Acadian Geology*, editions 1-4, 1855, 1868, 1878, 1891.

‡ Honeyman, D., *Quart. Jour. Geol. Soc., London*, xx, 1864; xxvi, 1870. *Trans. Nova Scotian Inst. Nat. Sci.*, 1866, 1882, 1886, 1887.

unravelling the stratigraphic sequence of the Silurian section exposed along the coast at Arisaig—a section unique because of its completeness, fossil contents, and decided European affinities. Later workers on the Silurian rocks have been Dr. H. M. Ami* of the Geological Survey of Canada, and Professors Schuchert and Twenhofel.† In 1886 Hugh Fletcher‡ of the Geological Survey of Canada published his final report on Pictou and Antigonish Counties, which gives the best general account of the district so far printed. Dr. Ami carefully described the Devonian strata of the area and published an account of the lower vertebrates obtained from them. Numerous other geologists have directly or indirectly added to the information relating to the region about Arisaig, which according to Honeyman became during his later life a household word in the homes of Canadian geologists.

Physiography.

Not only to the geologist and physiographer but to the casual traveler as well, the Arisaig-Antigonish district is a region of interest and delight. Possessing for Nova Scotia a maximum difference of relief, the area presents to the visitor during the summer months a delightfully green expanse of lowlands and rolling uplands, which flank a steep-scarped and generally wooded plateau. Trout streams, often several miles in length, occupy picturesque gorges in the plateau and uplands and flow in gently graded valleys across the lowlands. The plateau in places attains a height of 1000 feet and has an average elevation of about 800 feet. The uplands vary from 200 to 400 feet or more in height and the lowlands occupy the lower elevations down to about 50 feet above sea-level.

The plateau quite definitely belongs to the land forms recognized in the Maritime Provinces by R. A. Daly§ as being the remnants of a Cretaceous erosion surface of low relief, and the uplands belong to the secondary erosion surface of Tertiary time recognized by Daly in Nova Scotia. However, because of the resistance offered by the Silurian and Devonian rocks to erosion, the land surface above them was never reduced very nearly to a plain. The lowlands, consisting of stream valleys and seaward slopes, are the product of the earlier erosion cycles plus the differential erosion of glacial and recent time. They are best developed on the soft Carboniferous strata.

* Ami, H. M., *Trans. Nova Scotian Inst. Nat. Sci.*, i, new ser., pp. 185-192, 1892. *Bull. Geol. Soc. America*, xii, pp. 301-312, 1901.

† Twenhofel, W. H., and Schuchert, Charles, *this Journal* (4), xxviii, pp. 143-169, 1909.

‡ Fletcher, Hugh, *Geol. Surv. Canada*, II, p. 128P, 1887.

§ Daly, R. A., *Bull. Mus. Comp. Zoology, Harvard University*, xxxviii, pp. 73-103, 1901.

Glaciation.—Throughout the region mounds of unsorted clay and gravel are common, and in places are capped by sorted sands. On the plateau the ice of glacial times moved, as inferred from the direction of striæ on the rock surfaces, in a direction 10° east of south, but on the lower lands its course was somewhat varied as a result of the diversity of the topography at that time.

Recent movements.—Post-glacial rejuvenation is thought to be indicated by the presence of elevated terraces along the Northumberland Strait between 10 and 145 feet above the present sea-level. These terraces appear to be old sea beaches which have been modified only by the agents of erosion at work at the present time.

The geological record.

The geological history of the district is written in sedimentary records representing, with interruptions, the time from Upper Cambrian to Pennsylvanian. The following table will help to make the sequence clear.

SEDIMENTARY FORMATIONS.

Cenozoic.

Quaternary.

1. *Recent.*—Stream gravels and residual soils, modified glacial gravels.
2. *Pleistocene* or *Glacial.*—Unstratified clay-gravel deposits, red clayey marl.

Paleozoic.

? Pennsylvanian or Upper Carboniferous.

1. *Listmore formation* (Millstone Grit of Fletcher).—Light gray and red-brown sandstones, thin argillaceous shale, thin green conglomerate, etc. Thickness (Fletcher), 982 feet.

Mississippian or Lower Carboniferous.

1. *Ardness formation* (Carboniferous Limestone of Fletcher).—Brown and green sandy shale, ripple-marked sandstone and shale, gypsum (along the I. C. R.), and a compact bed of gray limestone. Thickness (Fletcher and corrected), 2045 “
2. *McAra's Brook formation* (Carboniferous Conglomerate of Fletcher).—Limy gray shale, green shale, cross bedded conglomerate, breccia and basal conglomerate. Cut by intrusive diabase sheets and dikes. Thickness (Fletcher), 1145 “

Devonian (Lower).

1. *Knoydart formation* (Upper Devonian of Fletcher).—Hard, fine-grained, red, sandy slate, and hard, gray sandstone, cut by small diabase dikes. Thickness (outcrops measured by Fletcher; probably should be doubled),.... 683 feet.

Silurian.

Arisaig series (Silurian of Fletcher).

1. *Stonehouse formation* (= more or less of Ludlow of England).—Red shale and limestones, argillaceous limestone and gray shales. Thickness (Twenhofel),..... 1075 "
2. *Moydart formation* (approximates the Louisville of United States, or Wenlock of England).—The red stratum or red shale, argillaceous limestone and shale. Thickness (Twenhofel),..... 379 "
3. *McAdam formation* (Rochester of United States or upper Llandovery of England).—Black shales and argillaceous limestone. Thickness (Twenhofel) + iron-zone probably 100 ± feet,..... 1120 "
4. *Ross Brook formation* (= Clinton of the United States, or lower Llandovery of England).—Green shale with thin sandstones, dark papery slates, etc. Obscure basaltic? intrusive. Thickness (Twenhofel),..... 833 + "
5. *Beechhill Cove formation* (= lower Clinton).—Sandstones, limestones and shales, resting on aporhyolite flow and volcanic breccia. Thickness (estimated from width of outcrop),.... 200 "

? Ordovician.

1. *Malignant Cove formation*.—Coarse, cross bedded, silicified conglomerates and grits; irregular dikes of basalt. Thickness observed (original thickness probably much greater),... 20 ± "

Upper Cambrian (Ozarkic).

Brown's Mountain group (included in Cambro-Silurian of Fletcher).

1. *Baxter's Brook formation*.—Red and gray sandstones and schists, red and green slates; intruded by rhyolite necks and dikes, quartz porphyry neck, diabase and basalt intrusives. Thickness represented estimated at..... 500 "
2. *James River formation*.—Flinty graywacke and grits, silicified banded slates; intruded by granite, rhyolite, diabase, basalt, and monzonite. Thickness represented probably 1 mile ±

Upper Cambrian deposits.—The oldest rocks known in the district are metamorphosed graywacke and slate of the Brown's Mountain group, which underlie the plateau areas and form the base for the younger formations. All of the younger sediments at one place or another rest directly upon the metamorphic rocks. The Brown's Mountain group may be divided lithologically into two divisions,—a thick lower formation of silicified graywacke, impure quartzite and gray banded slate known as the James River formation; and an upper division of crumpled red slate with some sandstone and schist, known as the Baxter's Brook formation. Oölitic hematite beds are found in the James River rocks near the base of the Baxter's Brook division and again at a lower horizon. The sedimentary origin of the iron ore is most probable from the consideration of the oölitic and sparingly fossiliferous character of the ore, its longitudinal extent, and its close association with definite rock horizons.* Some secondary concentration or transference of material may, however, have taken place.

So far as could be observed, the two formations have entirely conformable relations to each other, and on the evidence of *Obolus* (*Lingulobolus*) *spissus* and *Lingulella* (?) obtained from the upper iron-ore horizon (both from the ore itself and the associated schist), these rocks are proven to be of Upper Cambrian or Ozarkic age. The iron ore is likewise correlated with the Wabana ore of Belle Isle, Conception Bay, Newfoundland; but because of low grade and faulted condition it has not yet been commercially developed, although portions of it will probably be profitably mined sooner or later.

The characters of the Brown's Mountain sediments are thought to indicate that they were deposited in a shallow transgressing sea; the upper red slates were formed, perhaps, by the inwash of fine oxidized sediments from a land already reduced to moderate relief.

The present structure of the Upper Cambrian rocks consists of broad folds extending in a northeast direction, crossed by a few closed northwest secondary folds. The upper red slates are also intimately crumpled and folded as a result of the many intrusive bodies which have penetrated them.

Ordovician deposits.—Erosion agencies appear to have worn wide channels out of the Brown's Mountain rocks before the later sedimentary formations were laid down. The coarse cross-bedded conglomerates and grits of the Malignant Cove formation, occurring at Malignant Cove and to the south, were deposited upon the cleavage surfaces of the James River slates. Their deposition was evidently influenced by strong current

* For particulars see Woodman, J. E., Canada, Dept. Mines, Mines Branch, Report on Iron Ore Deposits of Nova Scotia, Pt. I, 1909.

action and their sedimentation characters, together with their general red color, suggest for these poorly sorted but well-worn deposits a continental origin.

Because of the orogenic disturbances suggested and because of the silicified character of its rocks, which are similar to those of the Brown's Mountain group, the Malignant Cove formation is thought to be a remnant of early Ordovician sedimentation.

Silurian deposits.—On the shore about one mile west of Malignant Cove, rocks of Silurian age rest unconformably upon an old rhyolite flow. As the Malignant Cove conglomerate contains fragments similar to, if not identical with, this rhyolite, it seems probable that the rhyolite flow was earlier than the conglomerate deposition and may have been at one time covered by the Malignant Cove formation. Be this as it may, but small isolated deposits of conglomerate now remain between the rhyolite flow-breccia and the sandy shales at the base of the Arisaig series.

The Silurian formations occupy an area about $1\frac{1}{2}$ miles wide, extending from Malignant Cove about 6 miles to the southwest along the shore. The 3,500 feet of sediments here represented consist in a generalized ascending order of argillaceous sandstone, black carbonaceous shales, arenaceous and argillaceous shales, a $2\frac{1}{2}$ foot bed of fossiliferous hematite, argillaceous limestones, and red shales. As previously shown by Schuchert and Twenhofel, the Arisaig series represent a period of time in Europe between the lower Llandovery and the Ludlow, and so far as they can be correlated with other American occurrences they represent the time interval between the Clinton of eastern New York and the Guelph of interior America. The sediments are thought to be the deposits of a shallow sea during varying conditions of clear and muddy waters. For the detailed description of the formations and list of their fossils the reader is referred to the work of Twenhofel and Schuchert cited above.

The Silurian formations are separated from the older rocks by a great fault having a probable throw of 3000–4000 feet. During the down-faulting, readjustment within the younger strata took place, resulting in crumpling, overturning, and many small faults which have divided the area into a number of blocks. Because of the soft, yielding nature of the strata the structure is but poorly expressed in the surface exposures.

Devonian deposits.—Red sandy slates containing some gray impure sandstone rest unconformably upon the Silurian strata to the southwest. They, too, have been downfaulted to the north-westward by the major dislocation of the region, and have suffered readjustment in the form of a synclinal flexure and minor faulting. Ami, who gave these the name of Knoydart

formation, has shown from Ostracoderm fishes obtained from the lower strata that the deposits may be correlated directly with the lower Old Red Sandstone of Europe. In origin the Knoydart formation is evidently continental and probably originated in large measure along the estuary of a Lower Devonian river.

Mississippian deposits.—Mississippian sedimentation is represented in the Arisaig-Antigonish district by the McAra's Brook and Ardness formations. The former consists of red conglomerates, sandstones, and sandy shales, and on the east of the area includes considerable thickness of micaceous gray sandstone and oil-shale. Remains of *Calamites* and fern-like impressions have been found in the oil-shale. Near the top the sandstone is limy and is apparently conformably overlain by the basal limestone of the Ardness formation.

The limestone which forms the lowest stratum of the Ardness formation is about 20 feet in thickness, and is succeeded by red sandstone and sandy shales, with some similar interbedded deposits of gray or greenish gray color. Along the south of the district, particularly in the valley occupied by the Intercolonial Railway, gypsum deposits probably 200 feet thick succeed about 200 feet of red sandstone and shale which rest upon the basal limestone. In the gray beds, particularly in those exposed along Northumberland Strait, fossil plants and carbonized wood occur in small amounts. The horizon-marking fossils are brachiopods obtained from the basal limestone exposed west of McAra's Brook. These are: *Productus doubtleti* Beede, very common; *P. dawsoni* Beede; *Pugnax* sp. undet.; *Martinia glabra* (Martin); and *Beecheria davidsoni* Hall and Clarke, rare. The limestone is thus shown on faunal evidence to be the same as that occurring at Windsor in the Windsor series. On the basis of the age determination thus made and the apparent conformability of the McAra's Brook and Ardness formations, they are both considered to be of Mississippian age.

? *Pennsylvanian deposits.*—Westward along the Northumberland Strait the Ardness formation is overlain by strata consisting of red and gray sandstone and sandy shale. Fletcher has termed these rocks the Millstone Grit formation; to avoid possible confusion with other areas in Nova Scotia, also thought to be equivalent to the so-called Millstone Grit, the present writer has distinguished the deposits in the Arisaig region as the *Listmore formation*.

So far as evidence goes in the Arisaig-Antigonish district, the Listmore formation overlies the Ardness conformably. In deference, however, to the determination of Fletcher, based on observations made over a wide area, the age of these strata is provisionally considered as Pennsylvanian, and a disconformity

is thus presupposed between the Listmore and the Ardness formations.

Summary of the Carboniferous deposits.—The three formations of Carboniferous age are much alike in their general characters. Although exhibiting minor flexing and faulting, the strata have not suffered great disturbances and overlap the great fault zone which affected the older formations. They generally dip with gentle gradients away from the rocks representing the older land. The many highly inclined contacts and the unsorted, breccia nature of the basal conglomerate, particularly along the scarps of the plateau consisting of Upper Cambrian rocks, suggest deposition of material near its source in previous troughs of erosion. The McAra's Brook conglomerates probably represent a phase of continental sedimentation which was later characterized by swampy conditions or, at any rate, non-oxidizing conditions, which favored the deposition of gray sandstone and beds of oil-shale and impure coal. Shallow marine or littoral conditions followed, culminating in the laying down of the basal Ardness limestone. Shallower waters again prevailed, and in isolated pans gypsum deposits collected as a result of excessive evaporation. As the Appalachian revolution began to affect the area, continental conditions finally superseded the littoral and continued not only during the deposition of the upper beds of the Ardness formation and the whole thickness of the Listmore formation, but according to the work of Fletcher lasted through the formation of the coal measures and the deposition of the Permian in the vicinity of Pictou and westward. The Windsor submergence was evidently the last of marine conditions for northern Nova Scotia.

Igneous Geology.

A number of eruptive and irruptive rocks are associated with the Upper Cambrian formations of the Arisaig-Antigonish district. The largest individual intrusion is that of fine-grained pink granite north of James River station. This is in the form of a stock, and as seen in surface exposures is dense and evidently represents conditions not far removed from the contact with the former cover. East of Malignant Cove, what appears to be an irregular monzonite stock is exposed along the shore. A neck of rhyolite forms the center of the Sugar Loaf Hill south of Malignant Cove, and rhyolite exposures in the vicinity indicate that erosion has laid bare considerable masses of an eruptive rock which had never quite reached the surface. The rhyolite grades into quartz porphyry containing large phenocrysts of orthoclase feldspar. The irregular porphyry bodies evidently represent intrusions similar to those of the rhyolite but more deeply eroded.

Through the surrounding rocks there are many small rhyolite dikes which appear to be connected with the general rhyolite intrusion. An *aporhyolite* or devitrified rhyolite flow probably 200 feet thick rests at the base of the Silurian section and is of historical interest because it was long mistaken for metamorphosed sediments on account of its banded structure. "Eozoon" forms were at one time reported from it.

None of the above intrusives is known to cut any rocks younger than those of Upper Cambrian age, and excepting the monzonite all are perhaps of related origin. Fragments of rhyolite are common in the Malignant Cove conglomerate, which is supposed to be of early Ordovician age, and fragments representing the James River granite and the monzonite are also thought to have been recognized in the conglomerate deposits. The available evidence thus favors the supposition that the intrusion of rhyolite, granite, quartz porphyry, and monzonite, and the extrusion of the aporhyolite flow took place during late Cambrian or early Ordovician time. Obscure tuff beds associated with the Upper Cambrian iron-ore zone indicate volcanic activity at a still earlier date, but the deposits are too much altered to shed much light upon the characters of such remote eruptions.

At a number of localities in the district diabase occurs either as irregular necks, which is the case at the Sugar Loaf Hill north of Antigonish town, or else as dikes, generally but a few feet across. In a number of cases the basic intrusives are of a basaltic rather than of a diabase nature. Unlike the igneous rocks already described, the diabase cuts rocks of all ages from Upper Cambrian to early Mississippian. Apparently the intrusion took place during one general activity, and so the diabase dikes and necks are probably of early Mississippian age.

Intimately associated with the diabase intrusives along the shore east of Arisaig Point is a long red dike of soft fissile character. It cuts the diabase dikes and the aporhyolite flow. This dike has been traced for nearly 3 miles, although numerous breaks occur in it, and part of the way two dikes are present instead of one. Studied microscopically, the red dike is seen to contain much iron oxide, but it evidently was originally composed of elastic material. It is thought to have been of a fine breccia nature, which may have originated during pulsations of material which reached nearly to the surface. In places the red dike is associated with basalt which it cuts. It is possible that the basalt and the red dike represent late phases of the diabase intrusion and are essentially of the same age.

Thus igneous activity represented in the Arisaig-Antigonish district is thought to have been confined for the most part to late Cambrian or early Ordovician time, and to the early part of the Mississippian period.

ART. XXIII.—*Jackson on the Phylogeny of the Echini*;* A synopsis by CHARLES SCHUCHERT.

IN this monumental monograph are established the phylogeny and classification of the Echini, including young and adult, fossil and living types, and "based on the sums of the characters and not on single characters." The volume also contains a revision of all Paleozoic Echini.

The splendid and fully illustrated work is dedicated to the great echinologist, Alexander Agassiz, and to Alpheus Hyatt, "my beloved master and friend, whose principles of research are the keynote of this memoir." Hyatt's principles are the stages in development, senescence, acceleration, and parallelism, and it has been Jackson's constant aim to compare these stages with the characters of more or less closely associated types.

Jackson began to study Echini in 1896 and during the past seven years he has devoted most of his time to a detailed study of the species and genera of this class of Echinodermata. He assembled in his private collection more than 40,000 specimens of Recent and Mesozoic Echini in all stages of growth, actually studying more than 50,000 specimens, so that he might thoroughly understand the Paleozoic species and their phylogenetic relations to the later forms. That he has succeeded the volume bears abundant evidence, for no class of invertebrates, as a class, has been wrought out with more care and philosophic insight.

One of the most important features of the work is a new method of determining ontogenetic stages of growth by noting how the plates are introduced ventrally, and in the localized stages among the plates dorsally. Echini are a particularly good class to study phylogenetically, because they have so many parts, all of which must be taken into consideration. This mass of detail furnishes constant checks and when all are in accord proves the accuracy of the resulting phylogenetic scheme.

Geological Occurrence.

Aldrovandus in 1618 was the first to figure a fossil echinoid from the Paleozoic and curiously one of the rarest of species and the oldest geologically, *Bothriocidaris globulus*.

The author recognizes 24 genera of Paleozoic Echini and of these but 4 are new to paleontology (*Hyattechinus*, *Loven-*

* Phylogeny of the Echini, with a revision of Palaeozoic species; by Robert Tracy Jackson. Mem. Boston Soc. Nat. Hist., vii, quarto, 491 pages, 76 plates, and 258 text figures, Jan., 1912.

chinus, *Meekechinus*, and *Pholidechinus*). Of good species there are 119 and of these 23 are new. Of *incertae sedis* and *nomina nuda* there are 3 genera and 34 named forms.

Ordovician.—The oldest and most primitive Echini occur in the Middle Ordovician of Esthonia, Russia, where the genus *Bothriocidaris* is found with 3 exceedingly rare species (1 in the Jewe and 2 in the Lyckholm formations).

Silurian.—The oldest American representative of the class was recently found in the Rochester shale of New York (*Koninckocidaris silurica*, n. sp.). In the Llandovery of England occurs *Maccoya phillipsiae*, while the lower Ludlow has furnished *Palaeodiscus ferox* and *Echinocystites pomum*.

Devonian.—Germany has in the Middle and Upper Devonian *Xenocidaris* (3 species), *Eocidaris laevispina*, and *Lepidocentrus* (3). In the Upper Devonian of New York is found *L. drydenensis*. In England occur *Lepidesthes devonians* and *Pholidocidaris ucvaria*.

Lower Carboniferous.—The Lower Carboniferous is the period of greatest development of Paleozoic Echini and in America alone there are 50 good species, with 31 more in Europe. In the Millsap formation of Colorado occurs *Miocidaris cannoni*, a new species and the oldest stratigraphically of the Cidaridae, the stock that gave rise to Mesozoic and later Echini. *Archaeocidaris* has 10 American species and 12 other forms occur in Europe. Other genera in America are *Lepidocidaris* (1 species), *Lepidocentrus* (1), *Hyattecthinus* (3), *Pholidechinus* (1), *Palaeochinus* (1), *Maccoya* (2), *Lovenechinus* (4), *Oligoporus* (5), *Melonechinus* (11), *Lepidechinus* (3), *Perischodmus* (1), *Lepidesthes* (6), *Pholidocidaris* (1).

Upper Carboniferous.—"In the Upper Carboniferous the Paleozoic Echini have dropped out with extreme suddenness and relatively few species are known." *Archaeocidaris* has 17 species in America and 2 in Europe. The only other form is the American *Lepidesthes extremis*, n. sp.

Permian.—The cidaroid *Miocidaris keyserlingi* occurs in Germany and England. Of *Archaeocidaris* there is 1 species in America, 1 in India, and 1 in Australia. The only other form is the American *Meekechinus elegans*, n. sp.

Types of variation defined.

Jackson states that next to stages in development variation is an extremely important subject as a basis in phylogenetic determinations. Echini are especially valuable on which to study variation, because in them variation can be so definitely expressed. It is seen in the introduction of columns, number of plates in a row, number of oculars that reach the periproct, etc.

"In order to appreciate variation it is of fundamental importance to be familiar with the characters of the associated species and genera of a case in hand, and also the developmental characters of the same. Variation may be fairly classified under five more or less distinct heads:

"1. *Arrested variation*, in which the variant retains characters seen in its own young and typical of the adults of more primitive allies, but characters which are usually eliminated in development. . . .

"2. *Progressive variation*, in which the variant has characters not typical of the species, but which are further evolved on the direct line of differential development, and are seen typically in more evolved nearly allied species or genera. . .

"3. *Regressive variation*, in which the variant takes on characters of the adult of some simple and more primitive type of the group. Such characters are not necessarily a repetition of youthful characters but may go back to a remote ancestry. An arrested variant in a sense is one form of regressive variation, but a regressive variant includes much more than arrested variation. To distinguish them, an arrested variant is one that has developed to a certain point as usual, and then failed to take on the later added characters typical of the species, so that, although an adult, it has immature characters. A regressive variant is one that has attained full characters and then in later life has reverted to youthful or primitive characters as an individual variation, or it is a variant that from youth has primitive characters not normally seen in the development of the species. . . .

"4. *Parallel variation* is where a character is taken on exceptionally which may be compared with characters normally occurring in some type of the group not closely connected, so that it cannot be genetically compared. . . .

"5. *Aberrant variation* is where a character is taken on which is quite abnormal, not to be correlated with the typical condition in associated forms" (pp. 18, 19).

Comparative Morphology.

Significance of abnormal symmetry.—Echini are remarkably constant in their pentamerous system, but Jackson found 71 variant individuals or on an average "a little more than one to a thousand. The variants are partially or completely trimmerous, tetramerous, and hexamerous. . . . The ocular plates seem to exert a controlling influence in the building up of the corona, as below and in immediate contact with the oculars originate the coronal plates, both ambulacral and interambulacral. In connection with each ocular is developed a whole ambulacrum, and, in addition, a half-interambulacrum

on either side. That is, while an ambulacrum originates on the ventral border of an ocular, each interambulacrum may be considered as composed of two halves, the plates of which originated on the left or right of the area in contact with the adjacent oculars. If this is true, then the loss of an ocular would cause a failure to develop of the plates that normally went with it, also an abnormal position of an ocular should cause an abnormal distribution of the associated coronal plates" (35, 36).

The "variations from the pentamerous symmetry can all be considered as monstrosities" (50).

Ambulacral areas.—The ambulacrum "is the most essential feature of a sea-urchin, and has a first importance in classification and morphology, on account of the varied structure that it presents" (53).

Interambulacral areas.—"The interambulacrum in Echini functions chiefly as a space filler and a bearer of spines and pedicellariae. The spines serve for protection and more or less in locomotion, and pedicellariae as grasping, cleansing, and protective organs. In spite of this secondary physiological importance, the interambulacrum forms a large part of the test of the sea-urchin in most types, and is of very great interest, especially in Palaeozoic genera. The interambulacral plates originate in direct contact with the ocular plates and quite independently of the genitals. . . .

"The full differential characters of the interambulacrum as of the ambulacrum are expressed at the mid-zone of the adult. Here are usually found the full number of columns of plates characteristic of the species, also the typical tubercles, spines, imbrication, or other characters which go to make up the specific description. The ventral border in the basicoronal zone represents the earliest formed plates and the youth of the individual, as far as it can be gathered from the study of an adult specimen, though the actually first formed plates may have been resorbed in development. Passing dorsally, with later added plates, new characters may come in until we get the full differential features developed at or about the mid-zone. Dorsal to the mid-zone we pass into the area of young last formed plates which have not yet acquired the full characters. Or again dorsally, we may find senescent features in the loss of columns of plates. Passing from the basicoronal row dorsally, we find in most Palaeozoic types, and many post-Palaeozoic as well, stages in development strongly marked, which stages can be correlated with the adult condition of simpler genera or simpler species within the genus. The interambulacrum in Echini has from one to fourteen vertical columns of plates in each of the five areas, which represents the least and greatest number known at present. There are

intermediate grades representing every step between this least and greatest specialization of the area, and it is a matter of great interest to follow the progressive series as represented by stages in development, and by adult types, to see how the progressive differential structure is built up. As the plates of the ventral border are the oldest or first formed of any plates seen in an individual specimen, and as the later added plates succeed one another as we pass dorsally, it might be thought that we could read stages in development as expressed by rows and columns of plates with ease and certainty, and such can be done in many types . . . Complications may come in, however, especially resorption of the base of the corona by encroachment of the peristome cutting off part of the ventral plates, and also rarely resorption within the corona, as exceptionally in *Arachnoides*, or differential growth of associated plates, which may separate plates originally in contact (*Echin-arachnius*)” (62-4).

Base of the corona.—“The characters of basicoronal interambulacral plates are the more striking and may be stated in brief. Where no plates have been removed by resorption, there is a single plate at the ventral border of the interambulacrum. The primitive type of this character is *Bothriocidaridaris*, which continues to build a single column. This same character of a single plate ventrally, but succeeded by two plates in the second row, is characteristic of the young of all modern regular Echini. . . . In the adult of most regular Echini the single plate and probably more have been resorbed by the advance of the peristome (*Eucidaris*). In the *Palae-echinidae* with many columns of plates, apparently only one plate has been resorbed, when we find two plates in the basicoronal row, . . . or in the *Archaeocidaridae*, several rows of plates may have been resorbed, and we find four plates in the basicoronal row. . . .

“In *Bothriocidaridaris* the basicoronal row consists of two high hexagonal ambulacral plates with pores superposed in each ambulacral area and one interambulacral plate in each interambulacral area. This same character is seen in young *cidarids*, young *Strongylocentrotus*, and *Echinus*, young *Salenia*, *Arbacia*, and *Phormosoma*. It is, I think, fair to call this a primitive character, and it represents what I (1896) described as the *protechinus* stage. The *protechinus* stage is comparable in other groups of animals to the *protoconch* of cephalous Mollusca, what I (1890) described as the *prodissoconch* of Pelecypoda, and to Beecher’s (1901) *protegulum* of Brachiopoda and *protaspis* of Trilobita. All are referable to what I termed (1890) the *phylembryonic* stage in development, a stage in which the differential characters of the class are established in ontogeny” (69-71).

Oculars and genitals.—"An ocular plate in Echini overlies an ambulacrum wholly and the two adjacent interambulacra in part on either side. Immediately on the ventral borders of the oculars all coronal plates originate. It seems that at this point the tissues exist which give rise to new plates. . . .

The five oculars are always present barring the excepted *Ponrtalesia*. The genitals overlie the interambulacra in part, but not the lateral borders of the same, and never reach the ambulacra. In some cases the genitals may not reach the interambulacra. Five genitals are typically present, but the posterior genital may be wanting (spatangoids) or one absent as an aberrant variation. . . .

"In the ancient *Bothriocidaris* the oculars are exceptionally large, relatively to the size of the animal; on the other hand, the genitals are exceptionally small, relatively the smallest of all known Echini. . . .

"No pores have been observed in genital plates in *Bothriocidaris*. It is possible they did not have genital pores, as such are wanting in the young of Recent Echini; more likely they were present, but do not show in external view. . . . Also no pores have been observed in ocular plates of *Bothriocidaris*. . . .

"Genital and ocular plates are rare in Palaeozoic types, yet excepting the Echinocystoida I am able to show them in all families other than the Archaeocidaridae and in most genera. After *Bothriocidaris* just considered, the leading character in the Palaeozoic is for all the oculars to reach the periproct, and to cover the ambulacra and in part the interambulacra on either side. Also the genitals reach the periproct, are larger than the oculars, and cover the interambulacra in part, but not wholly, because the lateral borders of the interambulacra abut against the next adjacent ocular on either side." In Paleozoic Echini, as a rule, "the ocular plates are imperforate. . . . In post-Palaeozoic Echini ocular plates have one pore not always visible externally (*Salenia*, *Arbacia*) and very rarely a second pore may exist as a variant. I have seen only two or three such" (86-89).

Systematic value of oculars.—"A close study reveals characters of importance to general morphology, to the evolution of the group, to the relation of the species in the genus and related genera, and to geographical distribution. Ocular plates present an excellent systematic character which has been largely overlooked. . . .

"Early in my studies of these plates it was seen that they had an important bearing, and observations were made on all available specimens of regular Echini, Mesozoic and Recent. In the fossils this is not always easy, as for purposes of study, all five oculars and genitals must be observed, and they are

frequently lost in fossils. I have succeeded, however, in making observations on something over 50,000 regular Recent and Mesozoic specimens representing 133 species. . . . The reason for making so many observations was that while the character of a species is usually gathered correctly from five or ten specimens, the variations seen in a large number present interesting data for comparative study. . .

"In Mesozoic regular Echini the dominant character is for all the oculars to be exsert, or excluded from the periproct. In the Recent regular Echini the young also have all the oculars exsert. In the adult all the oculars may be exsert or one or more be insert. While the exsert character of the young is like the Mesozoic, the becoming insert in development is the taking on of a character which in this respect is directly comparable to the dominant character of the Palaeozoic. . . .

"As becoming insert is a progressive character with development, species in a genus that have the greatest number of ocular plates insert may be considered in this respect more evolved than other species which have a less number (*Arbacia*, *Echinometra*). Also, as a matter of variation, individuals that have fewer oculars insert than is characteristic of the species may be considered arrested variants, and those that have more plates insert than is typical may be considered progressive variants. Such variants can frequently be compared directly with related species or genera where the fewer or greater number of oculars insert is a typical specific character (*Centrechinus*). Specimens of a given species from different localities present often quite striking differences as regards the number of plates which are insert, those from one locality having typically fewer oculars insert than those from a different locality. Such variation with locality may well be considered as indicating incipient species, as, where there is a difference, specimens from one locality must be more progressive or less progressive than those from another. . . .

"The number of oculars insert has been spoken of by previous writers as if it were a concurrent of age, and the largest specimens had the most oculars insert. My observations are directly opposed to this view. All the evidence goes to show that the full number of oculars that are to become insert are developed early in the life of the individual, and apparently later no change in this respect takes place. A series of specimens half the mature size or larger may in most species be safely accepted as showing the mature characters as regards oculars. This is on the basis of observations on 11,500 specimens of *Strongylocentrotus dröbachiensis*, all from one locality, Dumpling Islands, the specimens varying from very young to adult, and all measured and tabulated as later

described. With few exceptions it was found that the larger individuals in a species are typical as regards ocular plates, and that variations, both arrested and progressive, are more frequent in smaller individuals, often half grown as regards size" (90-1).

Genital pores.—"In very young Echini genital pores do not exist. . . Typically, in post-Palaeozoic regular Echini there is a single genital pore within the confines of each genital plate. . . . In the Ordovician *Bothriocidaris* genital pores are unknown. . . . In other Palaeozoic Echini genital plates typically have more than one pore to a plate. There may be two or three . . . or there may be three to five in a plate. . . . Instead of a few pores there may be numerous genital pores to a plate, even as many as ten or eleven. . . . It is possible that in types where fine madreporic pores are unknown, some of the larger pores served as madreporic openings. Otherwise all the pores in genital plates doubtless connected with genital glands, as in Recent Echini with accessory pores" (170-172).

Secondary value of genitals in classification.—"As seen from these studies, the genital plates have nothing to do with the interambulacrum, which develops on either side of the oculars. The genitals typically possess genital pores, and one of them possesses madreporic pores, but both of these structures may pierce other parts of the test. Genital plates may, therefore, be considered as structures of secondary importance, of much less morphological value than are the oculars" (173).

The lantern.—"It is believed that the structure of the lantern is of great value in systematic classification, and that the structure of its several parts presents characters that are of ordinal or subordinal value. As Dr. Mortensen pointed out (1904), the structure of the teeth, keeled or unkeeled, is 'a very important character, though it has hitherto received very little attention.' Besides the teeth there are other features of value. Briefly stated, the essential points are: teeth grooved or keeled; epiphyses narrow, or wide and united by suture; the top of the pyramids, as seen when the epiphyses are removed, a smooth floor, or pitted; foramen magnum deep, or shallow; angle of outline of the lantern depressed or erect; compasses present or absent" (177).

Classification.

The class Echinoidea Jackson defines as follows:

"The Echini, though possessing a wide range of structure, may be described as animals possessing alimentary, reproductive, nerve, and water vascular systems within an enclosing superficial pentamerous skeleton which bears movable spines. There are from two to twenty columns of plates in each of the

five ambulacral areas and from one to fourteen columns of plates in each interambulacral area. New coronal plates are formed at the ventral border of the five ocular plates, ambulacral pores pass through ambulacral plates, rarely (clypeastroids) in part between plates. The peristome in all but the Exocycloida bears from one to many rows of ambulacral plates, with or without non-ambulacral plates. There are five oculars (apparently in part or wholly wanting in some of the Pourtalesiidae), and five genitals or fewer, the whole being fused into a mass in certain types of Exocycloida. The genitals typically have each one or more pores as exits of the five interradially situated reproductive glands. In addition, typically, madreporic pores exist in genital 2, but are not recognizable in most Palaeozoic forms. The periproct is more or less plated, situated within the oculo-genital ring, or in irregular types outside of that area; the anus is in the periproct. The masticatory lantern is composed of forty pieces (or clypeastroids thirty pieces); it is wanting in adult spatangoids. Respiratory organs consist of Stewart's organs, peristomal or ambulacral gills. Locomotion is effected by ambulacral feet or by spines, or both" (200).

A key to the classification of the Echinoidea is given on pages 201 to 208. Other keys to the species of Palaeozoic Echini are given under the systematic descriptions.

Ancestors of Echini.—The author states that Echini "make no close approach to other classes of the Echinodermata. . . . What the ancestor of the Echini as a class was is unknown, but it might fairly be sought amongst the Cystoidea" (200).

Basis of classification.—All Echini recent and fossil are classified by Jackson on the basis of "the structure of the adult and the development of the same. . . . no single character has been followed." The characters taken into consideration are: the ambulacrum, interambulacrum, coronal imbrication, basicoronal plates, ventral resorption of corona, ocular and genital plates, periproct, peristome, Aristotle's lantern, perignathic girdle, spines and tubercles, gills and sphaeridia. "The relative value of these parts naturally differs in different groups of the Echini" (199).

The protechinus.—"The most primitive type of Echini, I believe emphatically, is Bothriocidaris. This view is based on the simplicity of its structure, and especially on the close comparison of this structure with that seen in the very young of all geologically later Echini known and the youthful characters retained at the ventral border in the adults of many types" (208).

"Each interambulacrum of Bothriocidaris consists of a single column of plates, which is represented by a single plate at the ventral border of the interambulacra in the young of all other

Echini. . . . there is ample proof that the interambulacrum begins with a single plate, as shown by Lovén (1874), and Mortensen (1903). . . . This structure with less evidence I correlated (1896) as a stage in development with the single column of plates in *Bothriocidaritis*, naming it the *protechinus* stage. As Palaeozoic types with many columns of interambulacral plates begin at the ventral border, the young, with a single plate representing a single column, and later add their several columns during development, it seems that *Bothriocidaritis* throws great light on the numerous columns there existent" (210).

Order Bothriocidaroida.—Of Echini the oldest and most primitive order is the *Bothriocidaroida*, found in the Middle Ordovician of Esthonia. The only genus, *Bothriocidaritis*, has 3 very small species, with 10 columns of hexagonal ambulacral plates, each with a pair of centrally placed podial openings, and but 5 columns of interambulacrals which may have small spines. Plates not imbricate. Periproct within the oculo-genital ring, which consists of 5 very large oculars and 5 very small genitals. Jaws present. It is out of this stock, the *protechinus* stage, that all regular Echini have evolved as follows :

Later Echini.—"The feature of Palaeozoic Echini is that they have more than two columns of plates in each interambulacral area. This is true of all known forms excepting *Bothriocidaritis* and *Miocidaritis* as far as the latter occurs in the upper Palaeozoic. Gregory (1897), Sollas (1899), and others have assumed that the most primitive form of Echini had many columns of interambulacral plates in an area, and several authors have considered *Palaeodiscus* as the most primitive known type. On this basis evolution would entail a loss of such parts, as our modern types all have two columns of interambulacral plates in an area. The evidence of development and adult structure is opposed to this view. At the ventral border of the young of all known modern types, and at the ventral border of the adult where not removed by resorption, we find a single primordial plate in each interambulacral area succeeded in the second row by two plates. There is no evidence in development of a larger number of columns dropping out to two in any known living form, or indeed, in any fossil form excepting as seen in senescence (*Perischocidaritis*), and in the little known *Tetracidaritis* of the Cretaceous. I, therefore, consider the Echini usually classed as the *Euechinoida*, with a geological range from the Lower Carboniferous to Recent inclusive, and comprising the orders *Cidaroida*, *Centrechinnoida*, and *Exocycloida* as next related to *Bothriocidaritis*. This view is based on structure and development. I am well aware of the intervening [great] geological gap, but can only appeal to the rarity of all forms in the Silurian and Devonian to account for the absence of intermediate types. . . .

"The order Cidaroida is placed as directly derived from the Bothriocidaroida without known intermediate forms. The Cidaridae as regards the structure of the young and adult are the least removed from Bothriocidaris of any known echinoid, living or fossil. The young have high hexagonal ambulacral plates with the pores of the pore-pairs superposed. Each interambulacrum has a single plate ventrally, succeeded by two plates in the next row. The peristome has a single row of primordial ambulacral plates which are like those of Bothriocidaris excepting that in that type there are two peristomal rows. The base of the corona has not yet been resorbed, exactly like adult Bothriocidaris. In young cidarids the genitals are large and oculars small and exsert, unlike Bothriocidaris. . . . The Cidaroida present distinctly a combination of Palaeozoic with modern characters" (211-2).

Order Cidaroida with 10 columns of simple ambulacral plates and 10 of interambulacrals. Coronal plates rarely imbricate. Represented in the Paleozoic by *Miocidaris* (1 species in the Permian Zechstein) of Germany, and another in the Millsap of Colorado. Order well represented from early Mesozoic time to Recent. Out of the Cidaroida was developed the

Order Centrechinoida, where the ambulacral plates are usually compounded of demi-plates. The stock arose in the Triassic and continued to Recent. This order divides into 3 new suborders: (1) *Aulodonta* (Triassic to Recent), with teeth of the lantern grooved, and with epiphyses narrow and not meeting in suture over the foramen magnum (*Hemicidaridæ*, *Aspidodiadematiidæ*, *Centrechinidæ*, and *Echinothuriidæ*); (2) *Stirodonta* (Jurassic to Recent), with the teeth keeled and with narrow epiphyses (*Seleniidæ*, *Phymosomatidæ*, *Stomopneustidæ*, and *Arbaciidæ*); (3) *Camarodonta* (Cretaceous to Recent) with keeled teeth and wide epiphyses meeting in suture over the foramen magnum (*Temnopleuridæ*, *Echinidæ*, *Strongylocentrotidæ*, and *Echinometridæ*). The last named suborder is the most specialized of modern regular Echini.

Order Exocycloida, or the irregular Echini, developed out of the *Stirodonta* in the Jurassic and persists to Recent. Here the periproct is always outside of the oculo-genital ring and lies in interambulacrum 5. "Assuming a monophyletic origin for the group, the three suborders present a striking series of structural departures from the regular Echini from which they doubtless originated. Considering the characters of the group as a whole in brief, the compound ambulacral plates and peristomal gills of the *Holactypina* and the auricles of that group and the *Clypeastrina*, the existence of keeled teeth, where teeth are known, and the presence of sphaeridia, are all characters which unquestionably associate the *Exocycloida* with the *Centrechinoida* and not with the *Cidaroida*, where these structures

are non-existent. Mr. Agassiz (1909) has shown that in the young of the spatangoid *Echinoneus* a well developed lantern exists. This discovery is of the greatest interest and importance, as previously teeth were unknown in this group. . . . Looking back to the *Centrechinoida*, we find that this type of lantern exists only in the suborder *Stirodonta*. Further, the attachment of muscles, as stated, occurs only in *Arbacia* and probably other members of its family. . . . I therefore consider the *Exocycloidea* as connected with the *Arbaciidae*, probably through some early common ancestral stock" (217-8). The *Exocycloidea* have 3 suborders: *Holactypina* (Jurassic to Eocene) with the ambulacral plates compound or simple and with the ambulacral areas not petaloid dorsally; *Clypeastrina* (Cretaceous to Recent) with more or less flattened tests, ambulacral plates simple and the areas petaloid dorsally, while the lantern is highly modified; *Spatangina* (Jurassic to Recent) with the ambulacral plates simple and the areas commonly petaloid dorsally but with no lantern nor perignathic girdle in the adults.

Order Plesiocidaroida, an aberrant and imperfectly known stock restricted to the Triassic (*Tiarechinus*), in which the periproct is central but the genitals are large and occupy most of the dorsal surface. There are 2 columns of ambulacrals and 3 of interambulacrals. Plates not imbricate. Base of corona not resorbed. "It is not closely affiliated with any other group" (220).

Order Perischoechinoida, arose in the *Bothriocidaroida* at least as early as the Silurian and persisted into the Permian. Corona and periproct regular in form and position, with from 2 to 20 columns of plates in each ambulacral area and from 3 to 14 in each interambulacral area. No perignathic girdle, the lantern muscles attaching directly to the base of the interambulacral plates. Embraces the families

Archaeocidaridæ (*Eocidaris*, *Archaeocidaris*, *Lepidocidaris*), with 2 columns of ambulacrals and 4 to 8 of interambulacrals, plates thin and imbricating, base of corona resorbed, and primary spines large; Devonian to Permian.

Lepidocentridæ (*Kouinekocidaris*, *Lepidocentrus*, *Hyattchinus*, *Pholidechinus*), with 2 columns of ambulacrals and 5 to 14 of interambulacrals, plates thin and imbricating, base of corona not resorbed, and all of the spines small; Silurian to Mississippian.

Palaeochinidæ or *Melonitidæ* (*Palaeochinus*, *Maccoya*, *Lovenechinus*, *Oligoporus*, *Melonechinus*), with 2 to 12 columns of ambulacrals and 3 to 11 of interambulacrals, plates not imbricate, some resorption of base of corona, only small secondary spines; Silurian to Mississippian.

In this family the genealogical relations of the genera are

clearly evinced by the structure and development of the ambulacra, an entirely new method of getting ontogenetic stages of growth (231).

Lepidesthidae (*Lepidechinus*, *Perischodomus*, *Perischocidaris*, *Proterocidaris*, *Lepidesthes*, *Pholidocidaris*, *Meekechinus*), "one of the most specialized of all groups of Echini," with 2 to 20 columns of ambulacra and 3 to 13 of interambulacra, plates imbricating and no resorption of base of corona, primary spines small; Devonian to Permian.

Order Echinocystoida (new), arose in the same stock that gave rise to *Perischoechinoida* but is an offshoot from a common early stock. Irregular in form with the periproct apparently eccentric in an interambulacrum. From 2 to 4 columns of ambulacra and 8 to 9 of interambulacra. Plates thin and imbricating, with the spines small. Lantern typically echinoid, but no perignathic girdle. Families *Palaeodiscidae* (*Palaeodiscus*) and *Echinocystidae* (*Echinocystites*).

ART. XXIV.—*The Belt and Pelona Series*; by OSCAR H. HERSHEY.

THE sedimentary rocks of the Coeur d'Alene Mountains in Northern Idaho were first systematically studied in 1903 and 1904 by Mr. F. C. Calkins, assisted by Messrs. W. A. Williams and D. F. MacDonald.* Although consisting chiefly of variable proportions of only two minerals, quartz and sericite, it was found practicable to subdivide them into six formations as in the following table:

Generalized Tabular Section in Coeur d'Alene District.

Name	Description	Approximate thickness in feet
Striped Peak	Sandstones, siliceous, generally flaggy to shaly; color mostly green and purple: characterized by shallow-water features, as ripple marks, sun cracks, etc. Top removed by erosion.	1,000 +
Wallace	Thin-bedded, bluish and greenish, more or less calcareous shales, underlain by rapidly alternating thin beds of argillite, calcareous sandstone, impure limestone; these underlain in turn by gray-green siliceous argillites. Ripple marks, sun cracks, etc., throughout.	4,000

*The Geology and Ore Deposits of the Coeur d'Alene District, Idaho; Prof. Paper U. S. Geol. Survey No. 62, 1908.

Name	Description	Approximate thickness in feet
St. Regis	Indurated shales and more or less flaggy sandstones; colors mostly green and purple; characterized by shallow-water features.	1,000
Revett	White quartzites, generally rather thick-bedded; interstratified with subordinate quantities of micaceous sandstone.	1,200
Burke	Light-gray, flaggy, fine-grained sandstones and shales, mostly greenish, with a variable amount of purple quartzitic sandstone and white quartzite. Shallow-water features throughout.	2,000
Prichard	Mostly argillite, blue-black to blue-gray, generally showing distinct and regular banding. Considerable interbedded gray indurated sandstone, upper portion characterized by numerous alternations of argillaceous and arenaceous layers, and by shallow water features. Base not exposed.	8,000 +
		<hr/> 17,200

My study of these rocks has been most extensive in the Wardner District, where I have mapped an area about $4\frac{1}{2}$ miles long and 3 miles wide. Here the Burke and Revett formations are thicker and more complex than elsewhere in the Coeur d'Alene region and I have found it practicable, in order to bring out the structure better, to make local subdivisions of the formations. I have also added another formation at the bottom of the series. This, the Cataldo formation, consists of at least 1,000 feet thickness of heavy beds, many of which are finely laminated and cross-bedded, of medium-grained quartzite of light lilac color, alternating with thinner-bedded strata of dull greenish sericitic quartzite. It is apparently the basal member of the Belt series and probably corresponds to the Creston quartzite of Daly. It does not appear at the surface nor in the mines of the Wardner District, but must underlie them at great depth unless cut out by intrusive rock. That Calkins did not intend to include it in the Prichard is proved by his mapping a small area of it as Burke.

The Prichard formation in the Wardner District is largely a dark gray to black argillaceous material in thin regular beds. Where a slaty structure is well developed, the rock resembles the ordinary black slates of other regions. Another type is a hard greenish-gray siliceous shale. Scattered through the formation, but most abundant in the upper part, are beds of

white quartzite, generally of coarser grain than quartzites in higher formations. I have no means of determining the thickness of the Prichard in this district, but I am not disposed to criticize Calkins' estimate of 8,000 feet for the Coeur d'Alene District as a whole.

At the top of the Prichard formation there is a rock made up of dark bluish-gray argillite and whitish arenaceous material in very thin alternating laminæ. This passes by transition strata into the Lower Burke division, the best section of which is on the southern side of Kellogg Peak. The predominating type is a greenish, thin-bedded sericitic quartzite, the darker green bands of which appear quite strongly chloritic. Layers of hard, white, heavy-bedded, poorly sericitic quartzite, 2 to 6 feet thick, alternate with greenish sericitic quartzite and are quite numerous, though they constitute a comparatively small part of the Lower Burke member. In this section there is not much purplish material, but elsewhere in the district, particularly in the Deadwood Gulch region, there is much purplish gray, thin-bedded quartzite and shale which locally may attain a thickness of several hundred feet, though generally interbedded with greenish layers. My impression is that they characterize the upper portion of the Lower Burke. Lithologically they are indistinguishable from the purplish gray quartzites and shales of the St. Regis formation except that, I think, they are harder and less shaly than the latter. These purplish gray horizons have given me more trouble in the mapping of the Wardner District than has any other type of rock. The thickness of the Lower Burke member is about 1500 feet.

The Upper Burke member consists of an alternation of thin-bedded, greenish, sericitic quartzites and heavy-bedded, white, nearly pure quartzites. The first type of rock is generally softer, thinner bedded, and of a lighter green than the typical greenish gray Lower Burke quartzite. The heavy-bedded white quartzites microscopically resemble the white quartzites of the Revett formation, but they break down rapidly under weathering agencies and give rise to much fine yellowish quartzite debris. Underground, they are in places hard and flinty and in others have lost the cementing material and become an incoherent pure white sand. I draw the base of the Upper Burke at the bottom of the first heavy bed of such quartzite; this is usually 30 to 50 feet thick, though in one section it is 300 feet thick. The thickness of the Upper Burke member is about 2,000 feet, making 3,500 feet for the Burke formation as against 2,000 feet for the formation in the eastern part of the Coeur d'Alene District as estimated by Calkins. My impression is that the thinning eastward is at

the loss chiefly of the Upper Burke, which I could recognize in the vicinity of Burke, but not near Lower Glidden and Revett lakes.

The Revett formation at the type section in the cirque walls overlooking Revett Lake consists of heavy-bedded, hard white quartzites alternating with much thinner beds of greenish sericitic quartzite, of a thickness, west of Lower Glidden Lake and on the west side of Twenty-two Mile Creek, of 1,000 to 1,200 feet. In the Wardner District the series is thicker and the greenish sericitic quartzites form a more important constituent. The Lower Revett is harder and more resistant to weathering than either member of the Burke. Its areas are characterized by a very stony soil, in many places taluses bare of vegetation, in which material there is an angularity not present in the debris from any other formation. In a good section in Big Creek Valley the thickness is 1,300 feet. The Middle Revett division is simply the highest prominent band of white, nearly pure quartzite; it is heavy-bedded and cross-bedded, weathers either white or yellowish, and has a habit of outcropping as a persistent precipitous ledge. It is generally 75 to 100 feet thick, but thins perceptibly in short distances, and may be practically absent from portions of the district. The characteristic rock of the Upper Revett is a rather thin-bedded, greenish, sericitic quartzite, similar to the thinner-bedded portion of the Lower Revett, though near the top it has several white quartzite beds and locally a few thin purplish gray bands; in fact, it resembles the Lower Burke. The thickness is about 900 feet. This gives the Revett formation a thickness of about 2,300 feet in the Wardner District.

Much of the St. Regis mapped by me in the district is the basal member, a rather hard, thin-bedded quartzite of gray and lavender colors. There is an alternation of green and purple-gray shales and thin-bedded quartzites. No complete section is exposed in the district, but I have adopted Calkins' estimate of 1,000 feet for the Coeur d'Alene District in general. The Wallace formation is confined chiefly to a large block between two great faults, the Osburn and Alhambra, and probably includes nearly all of the 4,000 feet thickness estimated by Calkins for the formation. The lithologic features are similar to those near Wallace and eastward, except that the quartzite beds are thicker and purer and there is less limestone. Although much of the formation is somewhat calcareous, the only limestone observed is a thin bed of blue-gray, nearly pure limestone in the Elk Creek basin. The blue-gray argillites weather to an orange color and the quartzites to a light red color. The Striped Peak formation has long since been eroded from all parts of the district.

Thus we may have a total thickness (including 1,000 feet of Cataldo quartzite) in the Belt group of strata remaining in the Wardner District of 19,800 feet. A geologist, whose past experiences with other alleged thick formations entitle him to take a critical view of the subject, has expressed the conviction that Calkins' estimates of the thickness of the Coeur d'Alene rocks, which were evidently derived by the measuring of sections at right angles to the bedding planes, are far too high. My estimates are based on a knowledge of the value that must be given to individual formations in making up the mass of certain fault blocks and are not dependent entirely on the original attitude of the bedding planes. I am not certain that the Prichard formation attains the 8,000 feet thickness assigned to it, but I am confident that the estimates of thickness of the other formations will in a general way stand the test of the most intensive study.

Elsewhere in the Belt area higher members of the series occur, and in the Belt Mountains and Mission Range of Montana they are nonconformably overlaid by Cambrian sediments. In the "Geologic Map of North America,"* besides the main area lying chiefly in Idaho, Montana, and British Columbia, a small area of Belt rocks is indicated in the Wasatch Range north of Ogden, Utah. The central portion of the Uinta Range is also mapped as Belt. The Wasatch area is presumably that which has been discussed recently by Mr. E. Blackwelder.† The prevailing rocks are variously colored quartzites or quartzitic sandstones. There are many thin beds of conglomerate and at several horizons hard shales and slates, chiefly dark purplish brown and bright green, though some are distinctly black and others rich maroon. A few thin beds of brown dolomite occur. Cross-bedding, ripple marks and sun-cracks are prevalent. These strata are referred to the Algonkian and are presumed to be overlaid nonconformably by Lower Cambrian quartzite 1,000 to 1,500 feet thick, and this by Olenellus-bearing shales and limestones. The base of the Cambrian quartzite is placed at a well-marked conglomerate.

During the first six months of 1905, I made an extensive geological reconnaissance of a portion of Eureka, White Pine and Elko counties in Eastern Nevada, particularly of the ranges on both sides of Steptoe Valley. I find in my notebook under date of May 16, 1905, the following generalized section :

* Prof. Paper U. S. Geol. Survey No. 71, plate 1, 1911.

† New Light on the Geology of the Wasatch Mountains, Utah ; Bull. Geol. Soc. Am., vol. xxi, 1910.

Paleozoic Section in Eastern Nevada.

	Estimated thickness
1. Blue, heavy-bedded, very fossiliferous, black-cherty limestone (Ruth).....	1,000 feet
2. Drab and light brown, massive cherty limestone with brown, coarse crinoidal limestone locally prominent in lower portion (Arcturus).....	700 to 1,000 "
3. Yellow and red, very fine-grained, soft sandstone alternating with light gray limestone layers; Upper Carboniferous (Arcturus).....	200 to 1,000 "
4. Light gray, drab and dark gray limestone, not very cherty, but with locally prominent red and yellow sandstone bed 10 to 200 feet thick.....	500 to 2,500 "
5. Brown and olive quartzite (Diamond Peak).....	0 to 100 "
6. Black, soft shale (White Pine).....	50 to 200 "
7. Light gray, massive limestone.....	50 to 100 "
8. Black shale and red and white quartzite.....	100 to 200 "
9. Dark brown, dark lead-gray and black limestone; upper part Upper Devonian (Ely).....	1,000 to 2,000 "
10. White, hard, fine-grained quartzite (Eureka).....	100 "
11. Blue, thin-bedded limestone; Lower Ordovician.....	200 "
12. Dark brown, very fossiliferous and black, soft shales; Lower Ordovician.....	200 to 500 "
13. Blue limestone; Lower Ordovician.....	100 "
14. Light gray, imperfectly fossiliferous, thin-bedded, in part brecciated or conglomeratic limestone; Lower Ordovician..	2,000 "
15. Massive, blue-gray limestone with peculiar wavy bands in shades of blue....	500 "
16. Blue, thin-bedded cherty limestone.....	700 "
17. Black, fossiliferous shale and blue shaly limestone; Lower Cambrian.....	300 "
18. Blue and gray, heavy-bedded limestone.....	1,000 "
19. Dark blue limestone.....	50 to 100 "
20. Brown quartzite, green mica slate and blue limestone interbanded.....	300 "
21. Pink and white quartzite.....	2,000 "
22. Black slate weathering purple.....	150 to 1,500 "
23. White conglomerate (bearing jasper pebbles) and quartzite.....	100 to 200 "
24. Green slate.....	500 to 1,000 "
25. White and pink quartzite.....	500 to 2,000 "

	Estimated thickness
26. Green and black slate	400 feet
27. Brown and pink quartzite	300 "
28. Dark gray slate weathering dark brown	500 "
29. White, hard, fine conglomerate	50 "
30. Reddish brown, weathering dark gray, micaceous schistose slate	1,500 "
31. Black schistose slate	500 "
(Underlaid by intrusive granite)	
Total	15,550 to 23,850 feet

Small collections of fossils were sent to the United States Geological Survey, but I am so far separated from the reports on them, that I will merely make the statement that *Olenellus* was found in the limestones at a considerable height above the base, particularly in No. 17, if I remember rightly. At any rate, there is over 1,000 feet of undoubted Lower Cambrian limestones and shales. These pass by the transition formation, No. 20, into a great series of quartzites and slates, which appeared to me to be conformable throughout, though several conglomerate bands were observed. The lithologic characters are similar from the base of the limestones down, strongly suggesting a single series of sediments. There is no sharp break in the apparent degree of alteration, but in a general way a progressive increase in the metamorphism downward. Thus, Nos. 30 and 31 mark the approach to the stage of metamorphism reached by the crystalline schists. I was of the impression that the entire series represents continuous sedimentation and I classed all the strata under the Lower Cambrian limestone as also Lower Cambrian, though I recognized that this would give the Lower Cambrian period disproportionate length. Since becoming acquainted with the Belt rocks of Idaho, I have been impressed by a marked resemblance in a general way between them and this Nevada quartzite-slate series, not only in character of sediments but in degree of alteration. In both regions, quartzites predominate above and black slaty rocks below. The alteration (by regional metamorphic action) is slightly greater in the Nevada section than in that of Idaho.

This pre-*Olenellus* quartzite-slate series in Nevada may, doubtless, be correlated in a general way with the similar series in the Wasatch Mountains. Walcott regarded the latter as conformable and arbitrarily drew a line beneath which he considered the rocks as Algonkian. Blackwelder, however, has found evidence of a nonconformity that may be taken as a convenient plane separating the Lower Cambrian and Belt series. The same nonconformity may be marked by the white

conglomerate, No. 23, of my Nevada section. This would place about 6,250 feet of sediments in the Belt series. The lower members occur in a small area on the eastern slope of the Egan Range about 10 miles north-northeast of Ely. On the eastern slope of the same range about 4 miles north-northwest of Warm Spring, the section extends down to No. 26. In a belt extending from 5 miles north-northeast of Cherry Creek to 9 miles south of that town, the section extends down to No. 30. At Aurum, on the eastern slope of the Schell Creek Range, No. 24 is exposed, but 15 miles farther south the section extends down to No. 30. Nowhere is the base of the Belt sediments exposed. All the granite seen in Eastern Nevada is intrusive and probably post-Carboniferous in age, except in the range west of Clover Valley, where, under a limestone series, there were observed the following rocks:

1. Light gray calcareous mica schist intruded by white muscovite pegmatitic granite.
2. Gray mica schist.
3. White, coarse-grained micaceous quartzite
4. White micaceous quartz schist.
5. Dark gray, coarse biotite gneiss and schist.
6. Light grey granitic gneiss, varying to a slightly sheared, fine-grained granite.
7. Gray, medium-grained sheared granite.

I have no doubt that these rocks are Archean in age. The Belt series and a large part of the Paleozoic section are absent.

Blackwelder, in the paper already cited, argues that the Algonkian sediments in the Wasatch region were deposited "chiefly by rivers on extensive plains in a climate which was semi-arid or at least subject to dry seasons." He points out that "the regularity of the dip and the small amplitude of the cross-bedded structures implies currents moving in a single general direction, and currents of water rather than of wind." The ripple marks and tension cracks admittedly imply shallow-water conditions, with frequent exposure of the mud flats. He considers that "the imperfect assortment of the materials appears to indicate that the sediments were deposited rapidly, little time being given for that complete sifting of fine from coarse debris which is characteristic of the work of waves upon an open beach." He recognizes that the Algonkian (Belt) sediments of Idaho were probably deposited under conditions similar to those which obtained in the Wasatch region. Since reading his paper, I have been endeavoring to consider the rocks of the Coeur d'Alene District in the light of a possible origin from meandering rivers upon a great delta plain,* but

* Relative Geological Importance of Continental, Littoral and Marine Sedimentation, part 3; Jour. Geol., vol. xiv, pp. 524-566, 1908.

they do not impress me as typical river sediments. Rivers meandering on a plain leave channels which become filled with sediments and preserved. Nothing even remotely suggesting such a fossil channel has ever come to my attention in the Coeur d'Alene District. Furthermore, in my description of the Belt formations in the Wardner District I have taken pains to mention the existence in some of the formations of frequent bands of practically pure, white quartzite. These were originally beds of nearly pure fine-grained sand comparable with the St. Peter sandstone in the Mississippi basin. They prove a nearly perfect assortment of materials at frequent intervals ranging from late Prichard time to the close of the Revett period. They are not typical river sediments. It is difficult to understand how a river might deposit over a considerable area a bed of nearly pure quartz sand 100 feet thick. For these reasons I consider the fluvial origin of the Belt terranes not yet satisfactorily proved. Indeed, I am inclined to support the hypothesis that the sediments were deposited in a vast inland sea or lake into which large rivers carried great quantities of fine sediment, some of which was precipitated without perfect sorting, while some was brought under the action of currents that formed the white sand beds.

The Oro Grande series of marble, quartzites and slates in the Mohave Desert in Southeastern California* was correlated on lithologic grounds with the Lower Cambrian strata of Inyo County, California.† At that time I had not seen the latter, but I have since visited the White Mountain Range and continue to hold the impression that the Oro Grande series is the correlative of part of the Lower Cambrian of Inyo County. I want to call attention to the fact that the Oro Grande sediments have been altered by regional metamorphism to the same degree as the Lower Cambrian and Belt quartzites and slates of Eastern Nevada, excluding the lower two members of my section. They have a somewhat more altered appearance than the Belt sediments of the Coeur d'Alene District of Idaho; for instance, the slates are, macroscopically, more evidently micaceous.

At the Yellow Butte, about 12 miles by the California Northwestern railroad from Weed, and hence north-northwest of Mt. Shasta in Northern California, there is an "island" of older rocks rising through the Tertiary lavas. It consists mainly of a fine-grained hard white and gray quartzite in which are thin micaceous schists, the whole being unlike anything in the Klamath Mountains.

* Notes on the Later Cenozoic History of the Mohave Desert Region in Southeastern California; Univ. Calif. Publ., Bull. Dept. Geol., vol. vi, pp. 336-337, 1911.

† Some Crystalline Rocks of Southern California; Am. Geol., vol. xxix, pp. 286-287, 1902.

math region on the west, but resembling the Lower Cambrian and Belt quartzite-slate series of Nevada, and the quartzites and slates of the Oro Grande series in Southeastern California. With it is a granite, probably intruded in the quartzite.

In the Klamath region the Devonian rocks, including much igneous material, rest nonconformably on a series of crystalline schists that have been described by me under the names of the Abrams mica schist and Salmon hornblende schist.* In the summer of 1907 I greatly extended my acquaintance with this series. I found the hornblende schist member (which also contains fine-grained hornblende and micaceous gneisses) exposed in a narrow belt along Chinech Creek southeast of Orleans, and at Elk Creek near Happy Camp in Siskiyou County; in the latter area it attains a maximum width of several miles, with a prevailing eastern dip and an exposed maximum thickness of at least 5,000 feet. Near Seiad post-office there is an acid, white, pegmatitic granite, apparently very old (probably Archean), abounding in large inclusions of hornblende schist and gneiss from the Salmon (Chinech) formation, but chiefly a fine-grained, thin-bedded, hard, vitreous quartzite of pink, white, and light green colors, with some mica schist and traces of marble. The quartzites seemed to represent a formation not heretofore discriminated in the Klamath region. It may extend south to Marble Mountain.

Farther up the Klamath River is another belt of Archean schists. Under the Salmon hornblende schist, much of it rather coarse-textured, there is about 2,000 feet thickness of dark gray mica schists of the Abrams formation. Under this is 1,000 feet of light greenish (chloritic and, in places, actinolitic) coarse-textured mica schist, part of which appears to have originally been a granite, and somewhat resembles the lower member of the Pelona schists of Los Angeles County, California.† It is my impression that the various phases of schists do not maintain a regular sequence throughout the area of development of the Abrams formation. The chloritic and actinolitic schists probably represent igneous rock intruded at various horizons in the original sediments. By following the old Kelsey trail to Marble Mountain, I crossed the mica schist, then probably 5,000 feet of hornblende schist and hornblende gneiss, then intrusive granite and basic rocks, then fine-textured mica schists and micaceous and hornblendic gneisses accompanied by the peculiar, thin-bedded, white quartzite and white marble of the Seiad area. Higher there is a great series of

* *Metamorphic Formations of Northwestern California*; Am. Geol., vol. xxvii, pp. 225-245, 1901.

† *Some Crystalline Rocks of Southern California*; Am. Geol., vol. xxix, 1902.

dark-colored, in part black, mica schists, mica slates and fine-textured gneisses accompanied by marbles that extend to and constitute the prominent peak, Marble Mountain. Finally, the series is capped by 100 feet of the Salmon hornblende schist. At Scott Bar there is an area, probably a mile long and a quarter of a mile in maximum width, of light gray, coarse-textured gneiss that was originally an Archean granite, probably intruded into the Abrams sediments before the development of schistosity. Thence I traced the Abrams schists in a great belt through the Siskiyou Mountains into Oregon.

In discussing the Pelona schists, which I had mapped in an area about 20 miles long in Los Angeles County,* I suggested that they are of the same age as the Abrams mica schists of the Klamath region. Last year I became acquainted with another area of the Pelona series. It constitutes the greater portion of the Rand Mountains near Randsburg in Kern County, California. It has recently been described by Mr. F. L. Hess† as largely a gray mica-albite schist. In the Atolia scheelite district it is bounded on the southeast by a complex of Archean granitic and dioritic rocks. Hess says the main granite mass seems to be under and may be older than the schists of the Rand Mountains. I am inclined to agree with him, though it involves an overturn of the strata along the border. A narrow band of marble and limestone follows this border, except where the contact is faulted. In the gray schist area I noted bands of quartz schist, hornblende schist, chloritic schist, and actinolitic schist, characteristic features of the Pelona series. As the two areas are only about 60 miles apart, I correlate them with considerable confidence. I propose, further, to extend the name Pelona series over the Abrams and Salmon formations of the Klamath region. I believe this Pelona series has a definite time position in the geology of the Pacific Coast country, comparable with that occupied by the Belt series of sediments. It is the youngest important Archean series. Further, so far as my observation goes, it is the last sedimentary series preceding the Belt series.

Kellogg, Idaho.

* Univ. Calif., Bull. Dept. Geol., vol. iii, No. 1, pl. 1, 1902.

† Gold Mining in the Randsburg Quadrangle, California; Bull. 480, U. S. Geol. Survey.

ART. XXV.—*Absorption and Thickness of thin Films*; by
C. C. HUTCHINS.

THE here recorded observations were made in the course of an attempt to find a window for radiometric apparatus that would effectually close such apparatus against all convective air currents, and at the same time introduce less absorption than rock salt or fluorite. It was argued that since the absorption of a body is an exponential function of its thickness, the body being made very thin, the absorption would nearly vanish even if the coefficient of absorption were high.

As is shown below, it is an easy matter to prepare permanent films of comparatively large area having a thickness of one-tenth to one-twentieth of a wave-length of light, and an extremely small absorption even for very long waves.

Preparation of Films.

Make a collodion by dissolving gun-cotton in amyl acetate. Instead of gun-cotton I have used shavings from the transparent celluloid handle of a discarded toothbrush, and found the result almost as satisfactory. The collodion should be rather thick at first, then gradually diluted until the proper consistency is found by making trial films; then filter through cotton until it is perfectly pellucid.

For practice one may bend up a ring, say 5^{cm} in diameter, at the end of a stout iron wire, soldering it so that it may be smooth and flat; later, any desired support may be used.

Fill a large evaporating dish with clean water. Dip the rounded end of a glass rod in the collodion and touch the adherent drop to the surface of the water in the middle of the dish. The drop instantly spreads to a large disc on the surface of the water. The film quickly sets, by the evaporation of the solvent, so that at the end of a minute or so it may be removed to the support. Slip the wire ring under the margin of the floating film; bring the ring into contact with the film at the margin, then very slowly and steadily raise the ring to a vertical position, at the same time withdrawing it from the water. The portion of the film not on the support gathers to a tail at the lower edge.

The film is then hung up to dry, and as it does so it will be seen to show the Newton black all over its whole surface, being too thin to reflect much light. A little practice enables one to spread a film upon any desired support. When dry they are very strong and do not break from shock.

The films are transparent to long waves.

The transmission of the films for very long waves was tested as follows: A radiomicrometer was set up. Before the opening of this was placed a thin blackened copper tank containing water at room temperature. This tank could be raised and lowered in a frame by pulling and releasing a string. Behind the movable tank was a large cubical tank containing ice. The radiation was therefore from a body at about 22° to one at 0° , consequently the radiation maximum lies far out in the infra-red at wave-length $10\ \mu$. Exposures were made by raising the movable tank, as noted above, and the ratio of the mean radiomicrometer deflection with the film interposed to the mean without the film gives the transmission.

The following is a typical observation:

Temp. of movable tank	$22^{\circ}\cdot 2$
“ of stationary tank	$0^{\circ}\cdot 0$
Mean deflection with film	$138\cdot 9 \pm 0\cdot 23$
“ “ without film	$139\cdot 6 \pm 0\cdot 21$
Transmission	$0\cdot 995$

Several films have been tested in like manner, all showing an absorption of less than one per cent; whereas a plate of rock salt $0\cdot 4\text{cm}$ thick, newly and perfectly polished by Brashear's method, gave an absorption of 22 per cent under the same conditions. It would appear, therefore, that a nearly perfect window for radiometric instruments has been found, provided only that the instrument is not to be exhausted.

A thin coating of collodion may be of use in protecting the surfaces of salt prisms and lenses from moisture. I polished two plates of salt and coated one by flowing it with very dilute collodion. The two have been exposed side by side for two weeks. The coated plate is still perfect, whereas the uncoated clouded in a day or two. It is too early, however, to know if the protection is permanent. A thin collodion film does furnish a permanent protection of silvered mirrors against tarnish. A silvered mirror in this laboratory turns yellow in a week owing to sulphur gases from a nearby railroad, but when flowed with a very dilute collodion it remains untarnished. I have such a mirror that has been exposed for three years that is as perfect as when new. The films are so thin that they in no wise impair the optical qualities of the surfaces to which they are applied.

Thickness of the films.

It is of interest to know the thickness of these black films. One film where it is doubled back upon itself over the wire ring used as a support, thus giving a double thickness, showed

first order interference color of about wave-length $\cdot 000057^{\text{cm}}$. Taking the index of refraction of the material as 1.5, we have for the film thickness:

$$\frac{\cdot 000057}{4 \times 2 \times 1.5} = \cdot 0000059^{\text{cm}}$$

The thickness was also found thus: A loop was made at the end of a fine platinum wire. Three films whose diameters were 12, 14, and 11.5^{cm} respectively were gathered from the water on which they were formed into a small ball on the wire loop, the water pressed out, and the remaining material dried to constant weight.

The wire alone weighed	0.0218 ^{gm}
Wire with film "	0.0231
Weight of film	0.0013
Area of film	372 ^{cm²}

The density of a sample of the toothbrush handle from which the film was made was 1.136. From the above we get for the mean thickness of the film:

$$\frac{0.0013}{372 \times 1.136} = 0.0000026^{\text{cm}}$$

equal to one-twentieth the wave-length of green light.

Bowdoin College, July 1st.

ART. XXVI.—*The Mazon Creek, Illinois, Shales and their Amphibian Fauna*; by ROY L. MOODIE.

THE Mazon Creek shales have been noted for many years for the excellence of the fossils which are found in them. These fossils are, for the most part, plant remains, but occasionally animal fossils are found, usually in nearly perfect preservation. Among the vertebrates which have been recorded from these beds are about twenty-five species of elasmobranch, dipnoan, crossopterygian and acanthopterygian fishes. Nine of these species are founded on scales and will doubtless be subjected to revision later. Other vertebrates are represented in the amphibian fossils, of which there are, at present, ten species known. These ten species are distributed among eight genera, five families and four orders; thus showing the amphibian fauna of the Mazon Creek shales to be a diverse one. This diversity undoubtedly indicates a long antecedent history for the group. The genera and species, even nearly all of the families, are exclusively Mazon Creek forms, not being known from elsewhere in the world. From this we know that in the Pennsylvanian the Amphibia were already a sufficiently old group to have established themselves into distinct, widely separate geographic groups. Just how long it may have taken for them to so establish themselves is, of course, a matter for conjecture.

The larger amount of the material representing the amphibian fauna of the Mazon shales is in the Yale University Museum, where it had been gathered by Professor Marsh. The writer is indebted to the authorities of the Museum for the privilege of studying this interesting collection. Seven of the species of the Mazon Creek Amphibia are known only in this collection at Yale. Seven of the species are founded on considerable portions of the skeleton, and some of them show many soft parts as previously described by the writer.* Two species are known from nearly complete remains of three individuals. The ten species are as follows:

1. *Amphibamus grundiceps*, Cope, 1865. Three nearly complete specimens.
2. *Amphibamus thoracatus*, Moodie, 1911. One incomplete specimen.
3. *Micrerpeton caudatum*, Moodie, 1909. One complete individual.
4. *Eumicrerpeton parvum*, Moodie, 1910. Three nearly perfect forms.

* American Naturalist, xliv, p. 367, 1910.

5. *Mazonerpeton longicaudatum*, Moodie, 1912. One nearly perfect skeleton.

6. *Mazonerpeton costatum*, Moodie, 1912. One imperfect skeleton.

7. *Cephalerpeton ventriarmatum*, Moodie, 1912. Skull and anterior part of body.

8. *Erpetobrachium mazonensis*, Moodie, 1912. Humerus, radius and ulna.

9. *Spondylrpeton spinatum*, Moodie, 1912. 12 dorsal (caudal?) vertebræ.

10. *Erierpeton branchialis*, Moodie, 1912. Impression of mandibles, parts of body and hyobranchial bars.

These species have been arranged zoologically according to the following plan:

Class—Amphibia, Linné, 1758.

Subclass—Euamphibia, Moodie, 1909.

Order—Branchiosauria, Lydekker, 1889.

Family—Branchiosauridae, Fritsch, 1879.

Micrerpeton caudatum, Moodie.

Eumicrerpeton parvum, Moodie.

Mazonerpeton longicaudatum, Moodie.

Mazonerpeton costatum, Moodie.

Order—(?) Caudata, Dumeril, 1806.

Family—Cocytinidae, Cope.

Erierpeton branchialis, Moodie.

Subclass—Lepospondylia, Zittel, 1887.

Order—Microsauria, Dawson, 1863.

Family—Amphibamidae, Cope, 1875.

Amphibamus grandiceps, Cope.

Amphibamus thoracatus, Moodie.

Cephalerpeton ventriarmatum, Moodie.

Family—Molgophidae, Cope, 1875.

Erpetobrachium mazonensis, Moodie.

Subclass—Stegocephala, Cope, 1868.

Order—Temnospondylia, Zittel, 1887.

Suborder—Embolomeri, Cope, 1885.

Family—Cricotidae, Cope, 1884.

Spondylrpeton spinatum, Moodie.

It will be seen from the above arrangement that nearly all of the orders of extinct Amphibia are represented in the Mazon Creek fauna. Since these animals are the oldest known land vertebrates of which there are skeletons, and since the beds in which they occur have never received adequate

description, it was thought that it might be of interest to present a short discussion of these remarkable fossil-bearing beds.

The writer was enabled to spend a week studying the fossil beds of Mazon Creek last summer with the aid of funds from the Department of Zoology of the University of Kansas and the Elizabeth Thompson Science Fund. It is fitting to express, in this place, to Mr. J. C. Carr of Morris, Illinois, my appreciation of the favors shown me while collecting at Mazon Creek. My purpose in visiting the locality was primarily to collect Amphibia, but although several thousand nodules were examined, none contained amphibian remains. Mr. Carr has collected on Mazon Creek for more than thirty years and knows more of the conditions of fossilization and location of the various beds than any one else. It is, however, a significant fact that during all these years of assiduous collecting he has never found an amphibian nor a fragment of one. It was this fact, together with the further one that the Amphibia referred to above represent over sixty years collecting from these beds, which interested me in making the following comparative table of the rarity of the various kinds of organic remains found in these beds.

If we take 100,000 nodules as a basis for computation of the rarity of the various forms, something like the following will be the approximate result:

Of 100,000 nodules,
20,000 will be barren or contain only indeterminate fragments.
68,500 will contain plant remains.
7,500 will contain insects, Crustacea, myriapods, scorpions, spiders and other Arthropoda.
3,900 will contain fish coprolites or scales.
95 may contain fish or fragments of fish.
4 may contain molluscs.
1 may contain an amphibian.

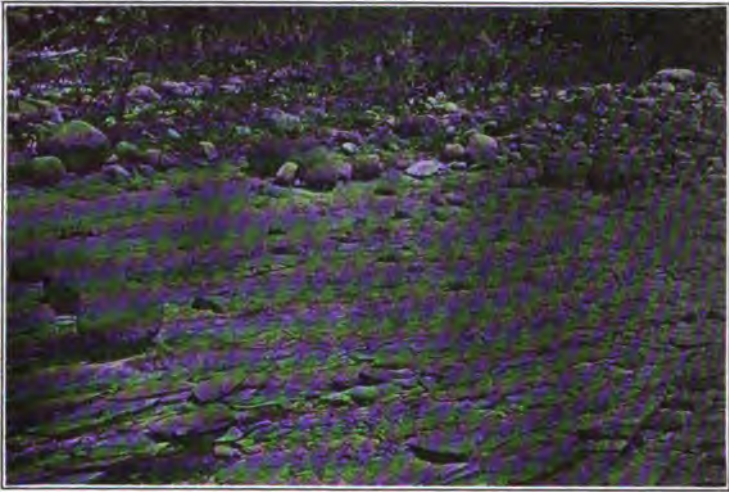
Total 100,000 nodules.

Perhaps even 100,000 is a little low as a basis of estimate. Mr. Carr was of the opinion that one nodule in every 500,000 might contain an amphibian. The table given above will, at least, be serviceable in giving an insight into the relative abundance of the various forms.

The beds where the nodules are usually collected occur along both banks and in the bottom of the creek (figs. 1 to 4) in two localities.

One locality, known as the Bartlett place, where I camped (fig. 1), is situated eight miles southeast of Morris, in Grundy county, Illinois, Wauponsee township; N. W. quarter section

FIG. 1.



The "Upper Beds."

FIG. 1. Nodules weathering out of the soft blue clay shale. Two quite long ones may be seen near the lower left hand corner of the figure, one of them still in place.

FIG. 2.



The "Upper Beds."

FIG. 2. "The stream bed is filled with glacial boulders, which form an excellent base on which to crack the nodules." Mr. J. C. Carr looking for nodules in the creek bed. He usually carries a basket and fills this, then sits down by a good boulder and cracks the nodules collected.

30; Twp. 33; Range 8; the land now being owned by Mrs. Emma Akerly of Wilmington, Illinois.

The fossil-bearing nodules occur throughout six to eight feet of shale, just above the coal, along both banks of the creek at the "upper beds," as the Bartlett place is called. They may be also seen in the creek bed, when the water is low, still embedded in the shale. With a common potato fork the shale is easily turned and the nodules come out for all the world like potatoes. Once in a while "pockets" are struck from which one may secure a peck or more of nodules. Nearly every nodule has a fossil at the "upper beds" but all of the fossils are not well preserved, possibly only one or two out of every eight or ten being worth carrying to the museum. The stream bed at the Bartlett place is filled with glacial boulders (fig. 2) which form an excellent base on which to crack the nodules. The nodules crack best when wet and it requires some skill and practice to crack them evenly. The nodules vary in shape and form from perfectly round ones, one-half an inch in diameter, to oval, elongate ones 17 inches or more in length. Many are quite irregular and it is soon noticed that the irregular nodules seldom have good fossils, often none at all. The nodules seem quite light, and in one place, where the stream curves, they are piled in a long windrow. On this pile were found several good specimens of Crustacea and many good plants, in nodules cracked open by the frost.

The fossils at the "upper beds" are localized into special strata. At one place in the upper part of the deposit in a red-dish shale one finds that insects are more abundant than they are lower down. The Crustacea appear to come from a definite locality in apparently the same shale. At the lower end of the deposits certain definite species of *Pecopteris* are localized. It is an interesting fact that one seldom finds a *Neuropteris* at the "upper beds." The most abundant fossils are various species of *Pecopteris* and *Annularia*. When specimens of *Neuropteris* are found they are usually discovered at the lower end of the exposures. In one place behind the "island" very blue nodules, hard and flinty, with sometimes well-preserved fronds of *Pecopteris*, are found quite definitely localized. These nodules are more likely to assume an irregular shape. These localizations of the various species of fossils are, of course, what we would expect from our knowledge of the manner in which the recent fauna and flora are distributed. There is, to be sure, more or less intermingling of species. The myriapods, as far as they have been found, are localized. Mr. Carr found three within a space of a few feet. But again these are found widely scattered. The exposures at the "upper beds" are about a quarter of a mile long. They disappear under a heavy ledge of sandstone.

FIG. 3.



The "Lower Beds."

FIG. 3. Looking south up Mazon Creek. The pebbly banks are covered with nodules and the stream bed is filled with them. They are easily collected by wading. Just above the rushes in the upper right corner the nodules are non-fossiliferous. Note the high bluff to the back. This continues along the west bank for some distance.

FIG. 4.



The "Lower Beds."

FIG. 4. A nodule just weathering out of the shale (at the head of the hammer). Others may be seen at the base of the slope. This shows the shales in position. The nodules contain, for the most part, species of *Neuropteris*.

At the "lower beds" (figs. 3, 4), so-called because farther down the creek, conditions are quite different from those just described. The west bank of the creek is higher and almost perpendicular, and the east bank is low and flat, the bluff being a quarter of a mile away, so that the chances for collecting from the shales are fewer. The bed of the creek, however, is wider and there are more nodules washed out. The most abundant fossil at this place is *Neuropteris*. The nodules at the upper end of the exposure are all, almost without exception, barren of fossils. The exposures here are of about the same thickness and extent as the "upper beds," though the species, contained in the nodules, are not so varied. Judging from the collections made while there, the Arthropoda are the more abundant in the lower beds. This is, however, a matter which needs further investigation.

Besides the place near Morris mentioned by Bradley there are no other localities known where the nodules are collected. Bradley* says of the Mazon Creek beds: "The outcrop (i. e., the Coal Measures) along Mazon Creek appears nearly continuous, but still I have not been able to satisfy myself as to the connection of the above beds with those of the lower part of the stream. The strata there developed consist of very variable sandy clay shales and sandstones, in some places becoming nearly pure clay shales, but containing many nodules of carbonate of iron. Pine Bluff, at the lowermost crossing of the Mazon, is composed of about forty feet of heavily bedded but rather fissile sandstone, partly nearly white, partly nearly ferruginous. Less than a mile up the creek, the lower part of this bed changes to highly argillaceous sandy shales, with occasional streaks and nodules of sandstone. The section is not quite continuous, but there is no distinct line of demarkation to separate these latter beds from the ferruginous sandy shales, twenty or thirty feet, of section 24, of township 33 north, range 7 east, which contain large numbers of the fossiliferous nodules of carbonate of iron, for which this locality has become famous. * * * * These nodules range from about two to ten feet above the main coal seam of all this region, the intervening space being occupied by the soft, blue clay shales, filled with fossil plants, which, at most points, overlie this seam. About a mile farther up the stream, coal has been dug in the bed and banks of the stream but is now abandoned. * * * * On the north side of the Illinois river, in the neighborhood of Morris, the coal outcrops in the banks of the canal, and in the stretch of lowland about one mile to the northward. The overlying beds are here mostly blue clay shales, with occasional irregular layers of sandstone. The iron nodules

* Geol. Surv. Illinois, IV, pp. 196-7, 1870.

above mentioned occur at the same level, but not in so great numbers as at the Mazon locality. The shales immediately above the coal frequently yielded magnificent specimens of fossil ferns and other plants."

The same nodules are thrown out of a coal mine at Braidwood, Illinois, and doubtless close search would reveal other localities where the shale is cut through in mining. The beds at both localities, along Mazon Creek, are slightly folded. This is especially true of the "upper beds," where a conspicuous fold causes the beds to disappear, to reappear in the bed of the creek a mile and a half north. This is directly across the large "ox-bow" bend of the creek. Mr. Carr said that he had followed the creek around the bend without discovering any new outcrops of the shales.

The beds at Mazon Creek were first explored in 1857 by Mr. Joseph Evans, who sent his specimens to Berlin, Germany, where they excited great interest. It was he who collected the type specimen *Amphibamus grandiceps*, Cope. Since the time of Mr. Evans many have collected at Mazon Creek, and without doubt the fossil-bearing nodules from the locality are more widely scattered in the museums of the world than are organic remains from any other one bed. The most eager and faithful collector at these beds has been Mr. J. C. Carr. He has presented many collections to schools and individuals, as well as furnishing material for many paleontologists. The writer is indebted to him for the presentation of an excellent series of nodules. The nodules at Mazon Creek will always be abundant, and the collecting will always be good so long as the creek continues to carry away the drainage of the region. We may thus hope to learn much, in the future, of the animals and plants of this wonderful locality. It is not possible, on account of the value of the land, to do extensive excavating, and this is not necessary, for the waters of the creek will, in time, make all the necessary excavations.

It is quite interesting to note in this place the discovery of a similar bed of fossil-bearing nodules in the banks and bed of Rock Creek near Twin Mounds Post-office, some 22 miles southwest of Lawrence, Kansas. The nodules have been known and collected for some time, and their similarity to those of Mazon Creek has been noted. The nodules at Twin Mounds contain identically the same genera and species of plants, insects, spiders, Crustacea, and a *Prestwichia* (*Euprops*) *danæ*, M. & W., as are found at Mazon Creek. There have been, so far, no evidences of vertebrates; even fish coprolites and scales are wanting. Further search may reveal these, as well as an interesting amphibian fauna. The beds at Twin Mounds will be fully described elsewhere, and further mention need not be made of them here.

The paleogeographic conditions of the beds containing the Amphibia at Mazon Creek, as well as those at Twin Mounds, are well represented in Doctor Schuchert's map.* A reference to this map, that of the Upper Pennsylvanian times, will show that the Mazon Creek deposits and the Twin Mounds deposits occur on the margin of the heavily shaded portion of the Upper Pennsylvanian sea. Doctor Schuchert suggests that the Twin Mounds beds represent a peninsula or a small island near the shore during Pennsylvanian times.

So far as our knowledge goes there is no evidence of vertebrate life of the uplands at this time. It was confined to the waters and to the borders of the waters. To be sure, we know very little of upland deposits, but there should be some suggestion of the vertebrates did they occur. It is a matter of the profoundest interest to witness here in the Upper Pennsylvanian the appearance of the earliest types of that branch of the animal kingdom which, in later epochs, was to dominate the entire world, some of these types returning to the water as a secondary adaptation. It is not possible for us to examine these lowly organized creatures without thinking that in them, or in creatures like them, lay the possibilities for the development of that race of animals to which we ourselves belong. Dr. Jennings has recently† expressed this idea, approaching the subject from an entirely different point of view when he says: "I was in actual material existence as a living organism, and indeed thousands or millions years old, when the pyramids were built, . . . " Is it possible for us to conceive that the habits of these amphibian creatures of the Mazon Creek region have left an impress on our own characters? If so, are they not worthy of our very careful attention?

Just what the details of the mode of evolution from these small creatures may have been we do not yet know, but patient and faithful search will reveal many new facts of the profoundest importance.

The University of Kansas, Lawrence, Kansas.

* Plate 84, Paleogeography of North America, Bull. Amer. Geol. Soc., xx, 1910.

† Science, N. S., xxxiv, p. 904.

ART. XXVII.—*An American Jurassic Frog*; by ROY L. MOODIE.

THE remains of Amphibia between the close of the Triassic and the opening of the Tertiary are among the rarest if not the rarest of fossil vertebrates. One can almost count on the fingers of one hand the species of Amphibia known in the post-Triassic, pre-Tertiary times. These are: *Hylæobatrachus croyii* Dollo of the Belgian Wealden; *Scapherpeton excisum* Cope, *S. favosum* Cope, *S. laticolle* Cope, *S. tectum* Cope; *Hemitrypus jordanianus* Cope, all from the upper Cretaceous (Laramie) of Montana, and Canada. So far as I know, other amphibian remains have not been described elsewhere from the formations mentioned.

Professor Marsh, in 1887, referred to some amphibian bones from the Como Beds* of Wyoming, calling attention to the previous mention of the species.† Again, in discussing the fauna of the Denver Basin,‡ he mentioned the amphibian where he says: "A batrachian (*Eobatrachus agilis*) and a peculiar fish (*Ceratodus güntheri*) have likewise been found in this horizon." The material has not been fully described, since all Professor Marsh's mention of them in 1887 is as follows: "More recently, various bones of small anourous amphibians (*Eobatrachus agilis*) have been found, the first detected in any Mesozoic formation."

Thus it is that, up to the present, the *Eobatrachus agilis* of Marsh has been a *nomen nudum*, and the discovery has been discredited. Recently through the kindness of Professors Schuchert and Lull of Yale University I have been permitted to examine the remains referred to by Professor Marsh, and find on examination that they are undoubted remains of Salientia, and of the modern type. There is no distinction, so far as I am able to observe by the most careful comparisons, between this *Jurassic frog* and the frogs and toads which are around us to-day. This is the more remarkable on account of the great age of the species. The Salientia have been suggested in the Pennsylvanian by *Pelion lyelli* Wyman, from the Coal Measures of Ohio, and attention has been directed to the salientian characters of the species by various writers. No intermediate forms are known and both the Jurassic and the Carboniferous forms are far too indefinite for any conclusions to be based on them as to phylogenetic descent. The transition took place in the Permian or late Pennsylvanian since this species *Eobatrachus agilis* Marsh has every identical character of the modern Salientia. The origin of the Salientia, like that of nearly all of

* This Journal (3), xxxiii, p. 328, 1887.

† Proc. Brit. Assn. Science, Aberdeen Meeting, 1885, p. 1033.

‡ Monograph U. S. G. S., xxvii, p. 508, 1897.

our great vertebrate groups, is still involved in mystery. The mystery is so great that it leads some to doubt the validity of the theory of evolution by gradual development. No distinct ancestral forms are known for any of the Amphibia save the Caudata. Smith Woodward has made the same statement in regard to the fishes and has emphasized the importance of the Mutation theory of DeVries as the paleontological record has thus far been read. The record is however still imperfect.

The present specimens seem to indicate a bufonid nature for the species. In fact I think we will be safe in locating the species in the family Bufonidæ and possibly even in the genus *Bufo*. It is entirely too soon for the species to be certainly placed in *Bufo*, since such a determination will have to await future discoveries of more complete material, especially of the pectoral girdle and the skull.

The reasons for placing the species in the Bufonidæ are simply on account of the well-developed condition of the lower end of the humerus and its apparently calcified condition. This is hardly more than an inference but it is an inference which has long been justified in Paleontology. Certainly the ulno-radial articular end of the humerus of *Eobatrachus agilis* is not the same as that of the modern *Rana pipiens*, or *Rana catesbeiana* and it does resemble the epiphyseal structures of calcified cartilage described by Parsons for some of the toads.

The specimens represent two individuals and by the following parts: One specimen, a lower end of a left humerus, somewhat smaller than the type; the other or *type* humerus; the lower end of a tibio-fibula; the entire left (?) femur; the entire right ilium, all, apparently, of a single individual excepting the humerus first referred to, which indicates a second frog though possibly of the same species. All of the specimens are from Quarry 9 of the Como Bluff in Wyoming.

The *humerus* (No. 1862 Yale University Museum) of the *type* as above stated is represented by the lower end only, this portion measuring 6^{mm} in length, by 2^{mm} in distal width, by slightly more than one half a millimeter in shaft diameter. The well-developed characters of the bone indicate a bufonid nature for the species as indicated above. The head, that is, the ulno-radial articular surface, is as distinctly marked as in all modern Salientia with which I am acquainted. The ball is apparently capped with calcified cartilage. Above the ball is a distinct pit for muscular attachments, precisely as in modern frogs. The shaft is quite slender and nearly circular.

The *ilium* (No. 1568 Yale University Museum) is quite peculiar and will possibly be sufficiently characteristic to sustain the validity of Professor Marsh's genus, *Eobatrachus*. The element is of the right side. It measures 10^{mm} in greatest length, by 3^{mm} in greatest width, by 2^{mm} in greatest thickness on the articular surface. The element is a slender rod, like the

modern salientian ilium, with the anterior end greatly narrowed and pointed; the pointed portion occupying one and one half millimeters. The shaft of the ilium is flattened laterally. It expands in width from a little less than one-half a millimeter to slightly more than three millimeters. The articular surface is marked by four pits which are the broken surfaces indicating the firm union of the elements of the pelvic girdle. The element is greatly thickened posteriorly, with a slightly developed, posterior, dorsal crest.

The *femur* (No. 1862 Yale University Museum) is quite distinctly amphibian of the salientian type. It is a slender rod of bone from which the epiphyses have been lost, leaving in their place pits occupying the ends of the bone; indicating the slight development of the endochondrium, as in all Amphibia. The lower end of the femur is divided into two surfaces by an imperfect partition, much as in modern frogs. The upper end is peculiar in having a well-developed crest which, in life, was undoubtedly capped by a large amount of cartilage. In the fossil state it has been preserved as a spine. The femur measures 12^{mm} in length, by 3^{mm} in distal width, by 1^{mm} in diameter of shaft, by 2.5^{mm} in proximal width.

The *tibio-fibula* (No. 1394 Yale University Museum) is represented by a portion of the lower end including 8^{mm} of the element. Its characters are so clearly those of the modern Salientia that a description is hardly necessary. The lower end is divided by grooves, one on either side, indicating the previous separation of the tibial and fibular elements, thus plainly showing that the frogs have had a long pre-Jurassic history.

The *humerus* of the other individual (No. 1863 The Yale University Museum) is similar to the one described for the *type*, though somewhat smaller. Like the *type* there is only the lower half preserved, measuring but slightly more than 4^{mm}.

The *Jurassic Frog* thus indicated by these imperfect remains was an animal about the size of *Bufo debilis* Girard of southwestern Kansas, and Texas; though possibly shorter in its bodily proportions as indicated by the short ilium.

The above description will indicate, without a doubt, that the *Eobatrachus agilis* of Marsh is the *oldest known frog*. It is hardly necessary to figure these imperfect remains since the above description has been written with the skeletons of several species of Salientia at hand and the comparisons are so exact, the characters so identical and the frog skeleton has been figured so many times that it hardly seems necessary. The specimens are in Yale Museum, where they may be seen at any time by anyone interested in a more direct generic and specific comparison. This has not been attempted in this short account chiefly on account of the lack of skeletal material of *Eobatrachus agilis* and on account of the lack of sufficient recent skeletal material.

ART. XXVIII.—*On the Hydrolysis of Metallic Alkyl Sulphates*; by G. A. LINHART.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxiv.]

II. *Methyl and Propyl Barium Sulphates.*

IN a previous article* it was shown both theoretically and experimentally that the rate of decomposition of ethyl barium sulphate in dilute hydrochloric acid solution is perfectly normal, and that it is approximately proportional to the strength of the catalyzer used. The purpose of this paper is to show the influence on the rate of decomposition of the salt of substituting a methyl or propyl group for the ethyl group. It was anticipated that the rate of decomposition would decrease with the increase in the molecular weight of the alkyl group, and this was confirmed by experiment, as is shown in Table II.

Preparation and Analysis of the Salts.—The salts were prepared as described in the first paper,† except that mechanical stirring was used during the preparation of the methyl and propyl sulphuric acids, as well as in their neutralization with barium carbonate; in the first case to prevent charring, in the second, to hasten the neutralization, as well as to prevent overflowing. A large crystallizing dish was used for the purpose.

The propyl salt thus prepared contains varying amounts of water of crystallization (one crop of crystals contained one molecule of water, another contained only one-half molecule of water) while the methyl salt thus prepared proved to be anhydrous. In fact all three salts, methyl-, ethyl-, and propyl barium sulphate, tend to lose their water of crystallization on standing. In one case the mother liquor from the methyl barium sulphate was allowed to stand over night, and on the next day it was found that the salt had crystallized in large rectangular plates ($1 \times 2 \times .2$ centimeters). All three salts may, however, be prepared with definite amounts of water of crystallization by allowing the crystals to remain in a Büchner funnel which is connected with the aspirator for several hours until the salt is fairly dry. It is then spread out on filter paper and kept in a dry place for a few hours. The salts thus prepared correspond to the formulæ:



Method of Hydrolysis.—The hydrolyses were made as described in the first paper.‡ Attention has been called to the fact that the precipitated barium sulphate chars on igni-

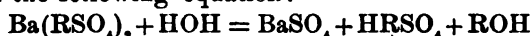
* This Journal, xxxii, 53.

† Loc. cit.

‡ Loc. cit.

tion, due to the inclusion of either alkyl barium sulphate, alkyl sulphuric acid, or possibly both. In the case of the methyl salt very little charring was observed, whereas in the propyl the whole mass turned black, so that the crucible had to be inclined and the lid placed in such a way as to allow a current of air to pass through during the ignition, until the barium sulphate became white.

Theory.—From theoretical considerations, which have been confirmed by experimental results, it has been shown that for every two gram equivalents of alkyl barium sulphate decomposed or of barium sulphate formed, one gram equivalent of alkyl sulphuric acid is formed, so that the concentration of the total ester $[Ba(RSO_4)_2 + HRSO_4]$ undergoing hydrolysis is, at any time t , not $(A-x)$ but $(A-x+1/2x)$, while the concentration of the acid accelerating the reaction is $(B+1/2x)$, as is shown in the following equation:*



from which was derived the mathematical expression for the velocity constant,

$$\frac{dx}{dt} = K(A-1/2x)(B+1/2x) \text{ or } K = \frac{2 \times 2.3}{t(A+B)} \log \frac{A(B+1/2x)}{B(A-1/2x)},$$

where A stands for the initial concentration of the alkyl barium sulphate and B that of the hydrochloric acid used, both expressed in gram equivalents per liter.

Experimental Results.

TABLE I.			T = 60°
BaSO ₄			
<i>t</i> in hours	in grams	in grm. equiv.	
B = 0.25 N HCl			
98.1	0.1352	0.0579	0.00782
191.2	0.2597	0.1113	0.00772
268.8	0.3637	0.1558	0.00772
335.7	0.4447	0.1907	0.00763
404.7	0.5285	0.2264	0.00761
481.0	0.6236	0.2672	0.00768
527.5	0.6752	0.2893	0.00768
α	0.7002	0.3000 = A	
B = 0.5 N HCl			
47.5	0.1270	0.0547	0.00791
95.5	0.2510	0.1075	0.00791
168.5	0.4228	0.1812	0.00791
265.0	0.6262	0.2683	0.00793
α	0.6932	0.2970 = A	

* This Journal, xxxii, 58.

TABLE I (cont.)

B = 1.0 N HCl

23.0	0.1312	0.0562	0.00852
47.5	0.2610	0.1118	0.00852
95.5	0.4840	0.2072	0.00852
143.0	0.6646	0.2848	0.00849
α	0.6932	0.2970 = A	

Ethyl Barium Sulphate

<i>t</i> in hours	BaSO ₄		T = 60°
	in grams	in grm. equiv.	K
	B = 1.0 N HCl		
20.4	0.1150	0.0493	0.00828
46.0	0.2490	0.1067	0.00828
69.5	0.3630	0.1555	0.00828
90.6	0.4596	0.1969	0.00835
118.5	0.5700	0.2442	0.00828
144.0	0.6670	0.2858	0.00832
α	0.7002	0.3000 = A	

Propyl Barium Sulphate

BaSO ₄				1 - 0
t	BaSO ₄		K	
in hours	in grams	in grm. equiv.		
B = 0.0625 N HCl				
72.0	0.0204	0.0088	0.00634	
211.0	0.0590	0.0253	0.00597	
379.0	0.1194	0.0512	0.00630	
545.5	0.1704	0.0730	0.00631	
783.0	0.2796	0.1198	0.00630	
930.0	0.3424	0.1467	0.00627	
1170.0	0.4356	0.1867	0.00607	
1435.0	0.5740	0.2459	0.00621	
1651.0	0.6794	0.2919	0.00625	
α	0.7002	0.3000 = A		
B = 0.125 N HCl				
93.5	0.0560	0.0217	0.00605	
210.0	0.1114	0.0477	0.00576	
586.5	0.3498	0.1456	0.00589	
823.0	0.4982	0.2134	0.00602	
971.0	0.5961	0.2554	0.00608	
1114.0	0.6720	0.2879	0.00598	
α	0.7002	0.3000 = A		
B = 0.25 N HCl				
25.0	0.0252	0.0108	0.00574	
91.0	0.0949	0.0407	0.00594	
191.0	0.1906	0.0817	0.00567	
223.0	0.2196	0.0949	0.00564	
378.5	0.3886	0.1665	0.00588	
564.0	0.5586	0.2461	0.00598	
α	0.7002	0.3000 = A		

B = 0.5 N HCl			
23.0	0.0482	0.0207	0.00604
66.5	0.1344	0.0576	0.00592
113.5	0.2200	0.0943	0.00575
169.0	0.3208	0.1374	0.00574
200.0	0.3744	0.1604	0.00575
250.0	0.4575	0.1960	0.00574
326.5	0.5734	0.2457	0.00572
α	0.7002	0.3000	
B = 1.0 N HCl			
44.0	0.2316	0.0992	0.00684
92.0	0.4574	0.1960	0.00687
138.0	0.6452	0.2764	0.00686
164.0	0.7394	0.3168	0.00685
α	0.8100	0.3470 = A	

TABLE II.

K for Esters in 1.0 N HCl

$\text{Ba}(\text{CH}_3\text{SO}_4)_2$	$\text{Ba}(\text{C}_2\text{H}_5\text{SO}_4)_2$	$\text{Ba}(\text{C}_4\text{H}_9\text{SO}_4)_2$
0.00852	0.00828	0.00684
0.00852	0.00828	0.00687
0.00852	0.00828	0.00686
0.00849	0.00835	0.00685
(A = 0.2970)	0.00828	(A = 0.3470)
	0.00832	
	(A = 0.3000)	

Summary.—The following conclusions are drawn from the experimental results :

1. Alkyl barium sulphates and alkyl sulphuric acids decompose extremely slowly in water solution even at moderately high temperatures.

2. The rate of decomposition of the salts is decreased with the increase in the molecular weight of the alkyl group, as is shown in Table II.

3. The inclusion of impurities is greater the larger the molecular weight of the alkyl group.

4. Fair velocity constants are obtained on the hypothesis that alkyl barium sulphates and the corresponding alkyl sulphuric acids are esters of similar stability in the presence of aqueous hydrochloric acid.

Experimental results have been obtained on the hydrolysis in acid solution of the calcium and strontium esters and also of the alkyl sulphuric acids, and in alkaline solution of the sodium, strontium and barium esters. These results will be published in subsequent papers.

ART. XXIX.—*On the Hydrolysis of Esters of Substituted Aliphatic Acids*; by W. A. DRUSHEL and E. W. DEAN.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxv.]

4. *Ethyl Esters of Glycollic Acid and of Methyloxy, Ethyloxy and Propyloxy Acetic Acids.*

PREVIOUS work on the hydrolysis of the esters of aliphatic acids has been reviewed in the first paper* of this series. The substances which had been previously studied were the methyl, ethyl and propyl acetates, the methyl and ethyl esters of chloracetic acid, and the ethyl esters of di- and trichloroacetic acids. The velocity of hydrolysis of isobutyl acetate had also been measured.

It was shown in this paper that the introduction of halogen into the acetyl radical lowers the rate of hydrolysis. It was also shown that the esters of different alcohols and any one acid differ but little in their velocities of hydrolysis in acid solution. The substances studied were the methyl, ethyl, propyl and isobutyl chlor- and bromacetates. In a second paper† it was shown that ethyl cyanacetate hydrolyzes more slowly than the chloracetate. From these results it would seem probable that the rate of hydrolysis bears some relation to the strength of the acids in esters and that this is in accord with the rule‡ stated by Nernst for the degree of hydrolysis of salts in general. Cyanacetic acid is about two and a half times as strongly dissociated as chloracetic, which in turn is about eighty times as strong an acid as acetic. It was shown, however, that this factor does not entirely account for the difference in reaction velocity of the esters.

In a third paper§ the results of work with alpha and beta chlor- and brompropionic esters are published. It was found here that the ester of the beta acid hydrolyzes more slowly than that of the alpha acid in the cases of both bromine and chlorine substituted derivatives. This is apparently an exception to the theory mentioned above, as the beta acids are weaker than the corresponding alpha acids.

A study has been undertaken recently to show the effect of the presence of hydroxyl and alkyloxy groups in fatty acid radicals on the rate of hydrolysis. The following esters are considered in this paper: ethyl glycollate, $\text{CH}_2\text{OH.COOC}_2\text{H}_5$; ethyl methyloxy-acetate, $\text{CH}_3\text{OCH}_2\text{COOC}_2\text{H}_5$; ethyl ethyloxy-acetate, $\text{CH}_3\text{OC}_2\text{H}_5\text{COOC}_2\text{H}_5$, and ethyl propyloxy-acetate, $\text{CH}_3\text{OC}_3\text{H}_7\text{COOC}_2\text{H}_5$.

* This Journal, xxx, 72.

† This Journal, xxxiii, 27.

‡ Nernst, Theoretical Chemistry, p. 521.

§ W. A. Drushel, this Journal, xxxiv, 69.

Preparation of the Esters.—The preparation of these esters was attended with some difficulty, largely due to the impossibility of employing any very effective methods of purification. The glycollic and methyloxy esters in particular are very soluble, rendering it impracticable to wash them with water. The last two esters of the series are more satisfactory in their preparation, although small yields were obtained by the methods employed.

The glycollic ester was prepared according to the method of Schreiner,* which depends upon heating together sodium glycolate, ethyl chloracetate and absolute alcohol in a sealed tube at 150° to 160° for a day. The tubes were then opened and the ester purified by fractional distillation. The first attempts to prepare glycollic ester by this method proved unsuccessful. There seemed to be a great tendency on the part of the ester to break down into glycollic acid and this was very difficult to remove, although its boiling point is 30° above that of the ester. The presence of small quantities of water or free acid in the glycolate appears to prevent almost entirely the formation of the ester. By the use of absolutely neutral and carefully dried sodium glycolate we were able to prepare a small quantity of the ester, which boiled at a constant temperature of about 155° and was proven free of halogen. The boiling point given in the literature is 160°, but the fractions we obtained boiling at this temperature generally contained free acid. It does not seem probable, however, that the presence of traces of glycollic acid can noticeably affect the hydrolysis, as it is one of the products formed in the reaction and is a very weak acid.

The alkyloxy acetic esters were all prepared by the same general method, the action of sodium alcoholate on ethyl chloracetate. The reaction proceeds according to the following equation:



In one case the mixture was allowed to react in ethereal solution, in the others an excess of absolute alcohol was used. The yields were rather poor, varying from 30 per cent to 35 per cent in the different cases. It seems possible that this may have been due to loss of ester while the excess of alcohol or ether was being distilled off, as the reaction is one which should go to completion.

The boiling points of the esters are given as follows: ethyl glycolate, 160°; ethyl methyloxy-acetate, 130°; ethyl ethyloxy-acetate, 152°, and ethyl propyloxy-acetate, 184.5°. The solubilities are not given in the literature. All but the propyloxy ester seem to be very soluble; the latter dissolves with a little difficulty in the quantities used in the hydrolysis.

* *Ann. d. Chem. u. Pharm.*, cxvii, 5.

Procedure.—The hydrolysis experiments were carried on in the thermostat described in the first paper* of the series. The temperature was regulated so that variations were never more than a tenth of a degree. The esters were hydrolyzed in 250^{cm}³ flasks, which were filled to the mark with decinormal hydrochloric acid and warmed to the temperature of the thermostat before starting the reaction. The esters were measured out in quantities of about 2.5^{cm}³ from a graduated pipette. At regular intervals 25^{cm}³ portions of the reaction mixture were removed by means of a pipette, run into cold water, and immediately titrated with decinormal barium hydroxide solution. Phenolphthalein was used as an indicator.

Experiments were carried on at 25.2°, 35°, and 45°, duplicates being obtained in all the cases. Calculations were made by using the titration formula for reactions of the first order. Figures are given below for the series which gave the most regular constants. Averages of duplicate series are also recorded.

TABLE I.

Hydrolysis at 25.2°.			N/10 HCl.		
Time (minutes)	Ethyl Acetate 10°K	Ethyl Glycollate 10°K	Methyloxy 10°K	Ethyl Alkoxy 10°K†	Acetates Propyloxy 10°K†
120	63.6	71.0	...	37.4	34.1
240	67.0	69.5	36.3	36.4	36.0
360	64.9	69.6	39.9	36.5	35.6
600	64.2	(79.8)	41.8	35.4	35.7
840	64.9	71.9	36.7	36.3	36.3
1380	65.6	69.9	38.2	36.5	36.9
2040	65.0	70.6	37.7	35.2	35.9
3180	---	---	36.0	---	---
Averages...	64.7	70.4	38.1	36.2	35.8
Averages... (duplicate)	64.9	68.5	38.9	36.1	35.8

Hydrolysis at 35°					
90	(155.5)	171.1	89.5	(80.5)	(71.8)
180	158.8	184.0	89.5	85.3	(78.9)
360	163.7	183.1	88.4	87.2	82.1
600	162.1	176.1	90.9†	88.3†	85.4†
900	162.8	168.0	90.4	87.2	85.3
1440	166.4	166.9	90.5	87.5	86.8
2160	(174.0)	160.5	92.3	87.9	86.8
Averages..	162.7	172.8	90.2	87.2	85.3
Averages... (duplicate)	162.6	166.2	90.0	87.5	84.0

* Loc. cit.

† These constants for 25.2° are calculated from series run at 25.0°. Time intervals are slightly different.

‡ Time interval, 700 minutes.

TABLE I (continued).

Hydrolysis at 45°.					
30	372	(366)	(252)	227	(174)
60	377	(360)	232	218	205
90	378	391	230	214	205
150	375	390	225	218	215
270	(338)	391	227	217	215
450	376	394	226	215	217
630	366	393	225	216	216
Averages..	374	392	227	218	212
Averages..	374	385	226	217	212
(duplicate)					

The constants in parentheses are not counted in the averages.

TABLE II. Summary.

Temperature.....	25.2°		35°		45°	
	10°K	10°K	10°K	10°K	10°K	10°K
	I	II	I	II	I	II
Ethyl acetate	64.7	64.9	162.7	162.6	374	374
Ethyl glycollate..	70.4	68.5	172.8	166.2	392	385
Ethyl methoxy- acetate	38.1	38.9	90.2	90.0	227	226
Ethyl ethyloxy- acetate	36.2	36.1	87.2	87.5	218	217
Ethyl propyloxy- acetate	35.8	35.8	85.3	84.0	212	212

The temperature coefficient varies between 2.3 and 2.5 for an increase of ten degrees. Average, 2.4.

Summary.

(1) Ethyl glycollate has a greater reaction velocity than ethyl acetate when hydrolyzed in acid solution. This would indicate that the presence of the hydroxyl group in an ester accelerates its decomposition.

(2) The methyloxy, ethyloxy, and propyloxy esters hydrolyze more slowly than the acetate, indicating a retardation caused by the presence of an alkyloxy group. This retardation increases with the size of the alkyl radical in the substituted group, the difference, however, being less marked between the ethyloxy and propyloxy than between the methyloxy and ethyloxy esters.

In a later paper we expect to show the effect of the presence of a second hydroxyl group in the acyl radical, and also the result of changing the substituted group from the alpha to the beta position. This work will involve the hydrolysis of esters of glyceric, lactic, and hydracrylic acids.

ART. XXX.—*An Electromagnetic Effect*; by S. R.
WILLIAMS.

UNDER the above caption Bowden* in 1895 described some interesting experiments on the behavior of a column of mercury in a magnetic field when carrying an electrical current. I have repeated his experiments with several variations, and inasmuch as Bowden closes his short report by remarking that some of the effects discovered by him are "difficult to understand," I may be permitted to offer an explanation of the effects and at the same time describe a very convenient method for measuring magnetic field strengths.

Bowden's Experiments.

Fig. 1 shows a sketch of the arrangement of Bowden's apparatus. A horizontal glass tube connected two troughs, A and B. Midway between A and B a vertical tube, V, was sealed into the horizontal tube. This was then filled with mercury as indicated and placed between the poles of an electromagnet. The dotted line *a, b, c, d*, shows the position of the pole pieces. The horizontal tube is normal to the magnetic field. If a current flows along the horizontal tube of mercury from A to B and the magnetic field is in toward the paper, then the mercury will rise in the vertical tube, i. e., in the same direction as the mechanical force acting upon a wire carrying a current in the same direction, \overrightarrow{AB} , when placed in a similar magnetic field. The glass tube is clamped in place and cannot move, hence the mercury moves with respect to the tube. Why it does is, perhaps, worthy of consideration.

It has been observed† that, if a heavy electric current is passed along a horizontal column of mercury, the column will break in two, then reunite to repeat the process of breaking again. This so-called "pinch-effect" has been explained from the viewpoint that the column of mercury is composed of a number of conducting filaments, each of which carrying a current in the same direction would have a mutual attraction for the other and, if this force is great enough, will crowd the filaments together and pinch off the column of mercury. If these filaments exist then, when placed in a magnetic field, as indicated in fig. 1, they would be acted upon as a flexible wire would be when carrying a current and placed in a magnetic field. Hence if this flexible wire were placed in the horizontal

* Bowden, *Phil. Mag.*, vol. xl, p. 200, 1895.

† Northrup, *Phys. Rev.*, vol. xxiv, p. 474, 1907.

tube it would be pressed up against the top of the bore of the tube and at the opening of the vertical tube would be bent up, making the wire to appear to rise in the vertical tube. If either current or field is reversed the wire would fall for the same reason. A good illustration of these filaments is found in the effect of an electric field upon some finely broken kernels of

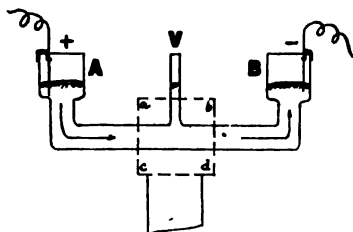


FIG. 1

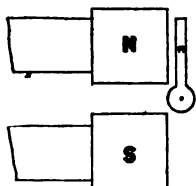


FIG. 3

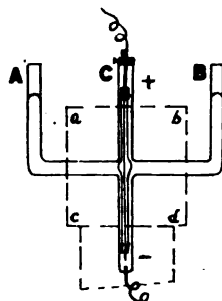


FIG. 6

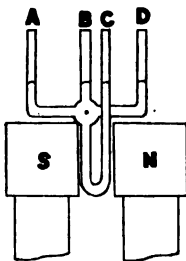


FIG. 4

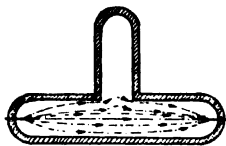


FIG. 5

halloysite, which is a compound of aluminium silicate and a very small amount of iron, nickel, cobalt, and manganese. I found that the small particles of halloysite (size of pinheads) when placed in an electric field such as one gets between the poles of a static machine, arrange themselves in filaments and, as one pulls the poles farther and farther apart, a chain of these

particles several centimeters long can be drawn along with the pole. Along these chains conduction takes place without any sparking. This, to my mind, is entirely different from the experiment described in Deschanel's *Natural Philosophy*, p. 67, Pt. III, by Professor Everett, in which the poles of a static machine are immersed in a bath of oil of turpentine. In this bath are thrown filaments of silk, and when the electric field is applied, the filaments arrange themselves parallel to the lines of tension, but do not take part in conduction. This

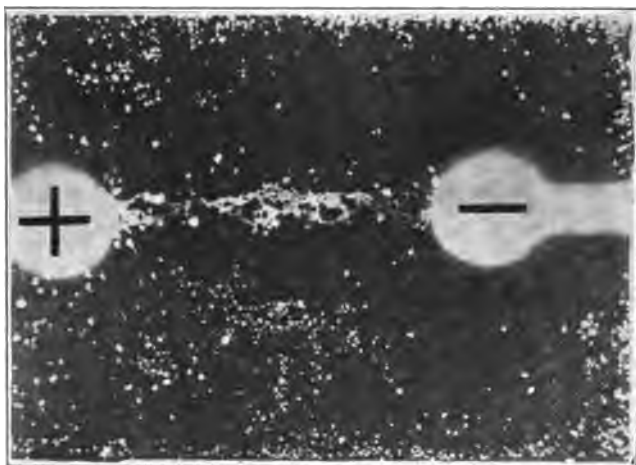


FIG. 2

last experiment simply shows the tendency of an elongated mass of a dielectric to set itself parallel to an electric field.

In fig. 2 is shown a photograph of the filaments of halloysite between the poles of an electric machine. A piece of photographic paper (velox) was placed directly under the poles and the broken halloysite piled around them on top of the paper. Keeping the electric machine excited, the negative pole was slowly separated from the positive. As the negative pole moved farther and farther away it dragged a chain of the particles of the halloysite with it, along which the machine was discharging without any sparking. When the poles were separated by a distance of about 10^{cm} an incandescent lamp was held over the poles and sensitized paper and an impression obtained as shown in fig. 2. From the standpoint of the filaments, all of Bowden's effects become intelligible. If one looks at the horizontal tube end on and places the tube between

the poles as shown in fig. 3, there is a rise of the mercury in the vertical tube no matter what the direction of the current and the magnetic field may be. Here the force acting upon the current in the mercury is normal to both the vertical and horizontal columns no matter what the direction of the current and the magnetic field. This lateral pressure on the sides of the horizontal tube acts hydrostatically and forces the mercury up in the vertical tube, as that is the only place that the pressure may manifest itself in a movement of the mercury.

In another form of tube he had four lateral tubes attached to the horizontal one. Fig. 4 shows the arrangement with horizontal tube end on. When the current flowed toward the reader and the field was in the direction indicated, the mercury rose in B, fell in C and momentarily rose in A and D. This momentary change in A and D was simply an inertia effect due to the changes in height of mercury in B and C.

In connection with this behavior of a mercury or liquid conductor carrying a current in a magnetic field, it is well to keep in mind the distribution of the lines of flow through the horizontal tube past the openings in the lateral tubes. This point was investigated in the following way: A conducting sheet of an electrolyte (acidified water) was arranged in the form which was the cross-section of the tube used by Bowden and shown in fig. 5. This cell was formed by sticking strips of hard rubber to a plate of glass. The lines of flow were obtained by the usual method employed in the laboratory, viz., using the secondary of an induction coil for the source of E. M. F. and a telephone receiver to locate the equipotential points. The lines of flow curve out into the opening of the lateral tubes as shown in fig. 5. After trying out the apparatus, similar in form to that used by Bowden, my attention was called to Lippmann's galvanometer* and its application by Leduc† and DuBois‡ in measuring magnetic fields. In principle their apparatus and Bowden's are one and the same. Fig. 6 is a schematic view of Leduc's apparatus. It differs from Bowden's in this respect, that the vertical central tube, C, extends below the horizontal tube, and the current is sent through the vertical column instead of the horizontal one. In Leduc's apparatus the column of mercury carrying the current was inclosed by two parallel plates, placed very close together with lateral openings for the tubes A and B, fig. 6. Bowden made his apparatus from glass tubing, and as a cross of the form in fig. 6 is easily made by sealing glass tubing together, it seemed worth while to see how satisfactorily a tube might be made for measuring magnetic field strengths instead of the flat cell used by Leduc and

* Lippmann, Jour. d. Phys. (2), vol. iii, p. 384, 1884.

† Leduc, Jour. d. Phys. (2), vol. vi, p. 184, 1887.

‡ DuBois, Wied. Annal., vol. xxv, p. 142, 1888.

more difficult to build. The measurements of the motion of the mercury column due to electromagnetic action were carried on by Mr. William Lyman, an advanced student in the department.

Mr. Lyman's Experiments.

Five tubes were made by ourselves in the laboratory and numbered 1, 2, 3, 4, and 5, respectively. The diameters in millimeters of the vertical central tubes and the side arms were as follows:

TABLE I.

No.	1	2	3	4	5
Vertical central tube	12.9	6.8	6.8	3.55	2.33
Side tubes	6.8	6.8	12.9	3.55	2.33

These tubes were placed between the poles of a small electromagnet, whose pole faces were $101 \times 76\text{mm}$ and the distance between them 46mm . The arrangement is shown in fig. 7. In fig. 8 is shown the relation between the change in height of

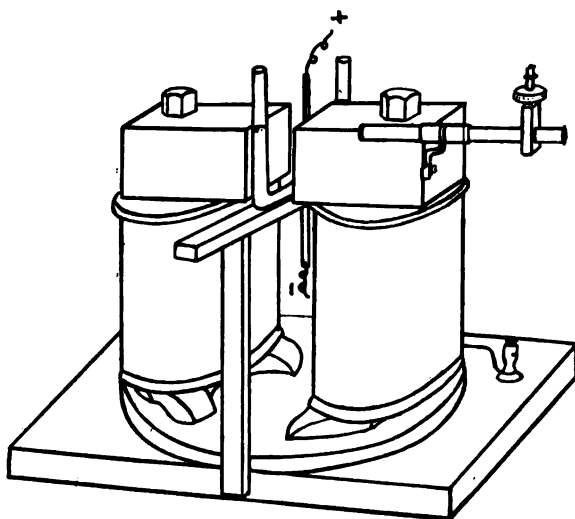


FIG. 7

the mercury column in one of the side tubes, and the field strength when the direction of the field was changed.* At first the results were very erratic. This was found to be due largely to the adhesion of the mercury to the walls of the tube. This trouble was remedied by placing a small quantity of glycerine on top of each meniscus. The glycerine behaved as

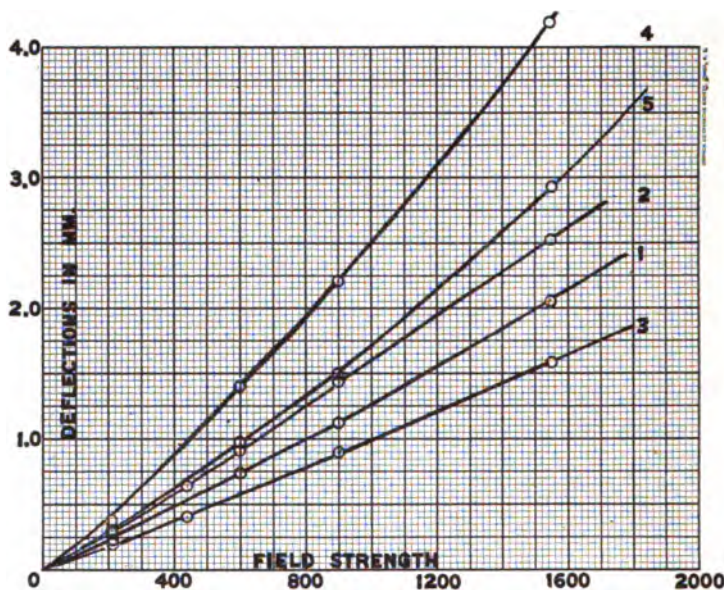


FIG. 8

a lubricant and the mercury moved along the tube like a well-oiled piston. With the glycerine covering all of the exposed mercury surfaces, the tubes could be left for weeks and would still yield consistent results. As a precaution the tubes were tilted in various directions each time they were used in order to get the glycerine down around the edges of the meniscus. The elevation and depression of the mercury column was read by means of a microscope and micrometer eyepiece in the case of tubes 1, 2, and 3, while a telescope and micrometer eyepiece were used for tubes 4 and 5.

Discussion of Results.

From the curves 1, 2, 3, and 4 it would appear that the smaller the tubes the more the mercury was displaced. Curve 5, however, contradicts this, and all of the curves point to the

* Fifteen amperes flowed through the vertical central column of mercury for all the values given.

reason why. As the tubes get smaller and smaller there is a greater departure from a straight-line variation of the displacement of the mercury with field strength. It is evident that the friction of flow of the mercury in the tubes is the cause of this variation from the straight-line law because the frictional forces become larger the smaller the bore of the tube. In curve 5 the frictional force has become so large that it reduces the amount of the displacements for the different field strengths to values lower than that in curve 4. One may conclude that some tube with dimensions between those of 4 and 5 would give a maximum displacement for the field strengths used in this work. If the frictional force is a constant, then all of the curves shown in fig. 8 will become practically straight lines beyond certain field strengths. The curves indicate this to be true.

The results obtained from these five tubes show that this is a simple and accurate means for measuring magnetic field strengths over wide ranges. No difficulty was experienced in measuring fields as low as 50 gauss. In actual practice we calibrated the tubes with a solenoid whose field was known, and then used the tube between the poles of the electromagnet whose field was to be determined. This eliminated the difficulty spoken of by those who have used Leduc's form of apparatus, viz., that the thickness of the conducting sheet of mercury must be known with great accuracy if one is to calculate the field strength from the amount of displacement of mercury, the current strength, and the dimensions of the tube.

If one can do sufficient glass-blowing to put together glass tubing as shown in fig. 6, an instrument can be easily and cheaply made which, when calibrated, may be used for accurately measuring unknown fields, and this without knowing any of its dimensions.

Summary.

1. This paper has attempted to explain the mechanism of this electromagnetic effect by assuming that in a liquid conductor we have a bundle of conducting filaments. The current flowing through these in a magnetic field will behave as it does in a flexible conductor in a magnetic field. In any case, whether we are dealing with conduction through gases, liquids, or solids, the effect obtained is due to the reaction between the magnetic field produced by the moving charges and the field in which the charge is moving.

2. This work has developed a simple and accurate method for measuring magnetic field strengths.

Physical Laboratory,
Oberlin College, Oberlin, Ohio,
March, 1912.

SCIENTIFIC INTELLIGENCE.

I. PHYSICS.

1. *The Growth of Air Bubbles at the Walls of a Beaker containing a Liquid, when the Gas at the free Surface is not air*; by C. BÆUS (communicated).—When water is poured into a beaker in air and an artificial atmosphere of hydrogen is then allowed to rest on the surface, it is surprising that the invisible air bubbles, which abound at the surface of all solid parts under the liquid, gradually become inflated to a relatively enormous size. They may be finally lifted off by their buoyancy. All submerged objects, notably wire gauze, become coarsely jeweled in the lapse of time; but the bubbles do not reappear when shaken off. This, however, is the second stage of the phenomenon. If the bubbles are not forcibly removed, they will of their own accord ultimately vanish by contraction.

Clearly the phenomenon as a whole is a case of the diffusion of hydrogen, through water, into the space indicated by the original microscopic air adhesions; but it is not at once evident why hydrogen should diffuse from top to bottom; *i. e.*, *against* the hydrostatic pressure gradient of the liquid. Nor does it appear why it should afterwards reverse the process; for the phenomenon is quite as evident for columns of water a foot or more high, or for large bulks of air under hydrogen. The explanation, which I have given, is as follows: Let h be the head of water above a given small air bubble, and B the barometric pressure. At the outset, therefore, the pressure of the hydrogen is B and that of the air underneath, $B + h\rho g$, in the usual notation. The pressure urging diffusion is thus initially from hydrogen into pure air B , and for pure air into hydrogen $B + h\rho g$. But as the diffusion proceeds, the gas within the bubble is no longer pure air, but a mixture of hydrogen and air, corresponding to the partial pressures p and p' ; so that throughout the experiment $B + h\rho g = p + p'$. Now p' continually diminishes from above atmospheric pressure, as the air escapes from the bubble, while p continually increases from the influx of hydrogen into it. The time must, therefore, come when $p' = h\rho g$ or $B = p$, at which the influx of hydrogen must cease altogether. When p' diminishes further, owing to the escape of air, it follows that since $p' < h\rho g, p > B$. In other words, both hydrogen and air afterwards escape from the enormously inflated bubble, until it vanishes.

In this way the very curious result is brought about of the apparent diffusion of a gas against hydrostatic pressure into an infinitesimal air bubble, until the latter is inflated to a bead, and thereafter of the reversal of diffusion and deflation—all in a continuous sequence of phenomena.

Brown University, Providence, R. I.

II. GEOLOGY AND MINERALOGY.

1. *First Annual Report of the Director of the Bureau of Mines*, JOSEPH A. HOLMES, for the fiscal year ended June 30, 1910. Pp. 57. Washington, 1912.—The first annual report from the Bureau of Mines gives an occasion for reviewing briefly what has been accomplished since it was established by act of Congress in July, 1910. Prior to that time the work in this field had been carried on under the auspices of the U. S. Geological Survey. The desirability, however, of increasing the health, safety, economy and efficiency of work in the various lines of mining and in the metallurgical industry has led to the separate development of the Bureau as now constituted. From the start the work has been carried forward with energy and efficiency and has only been limited by too small pecuniary support.

The scope of the work may be partially appreciated from the amount of money expended. This was a little more than \$500,000 in all for the year ending June 30, 1911. Of this sum \$310,000 was devoted to the investigation of accidents in mines, \$100,000 to the testing of fuels, and \$79,000 went to the expenses of administration, laboratories, etc.; while smaller sums were devoted to making public reports and to mine inspections.

The work of the Bureau is three-fold, including investigations as to mine accidents, of fuels and those in special technologic lines. The investigations relating to mine accidents have had a wide scope and have already accomplished important results, although with more liberal support they can be much extended. They look to the development of conditions which shall make work in mines as safe and healthful as possible and reduce accidents to a minimum. The Bureau has been also called to do much rescue work when bad accidents have occurred. The magnitude of the interests involved will be seen from the statement that there are 700,000 coal miners in the country connected with some 15,000 mines, out of which 500,000,000 tons of coal are produced annually. It is not to the credit of the country that the number of men killed per thousand in 1910 was more than four times what it was in Belgium, double what it was in Prussia and more than twice what it was in England. In metal mines accidents are nearly as frequent while health conditions are worse; the latter is also true in metallurgical plants.

The fuel investigations have been conducted with the object on the one hand of ascertaining whether the supplies purchased by the Government conformed to the contract specifications and in addition extended to the general character of coals, lignites and other mineral fuels belonging to the Government. Connected with this subject is that of the general prevention of mineral waste in all lines, which greatly needs scientific treatment.

Besides the administrative headquarters in Washington, the Bureau has also an experiment station in Pittsburgh with good

facilities for carrying on the various lines of experimental work, both physical and chemical, in testing fuels, explosives, etc. The publications of the Bureau include an extended series of bulletins, also a number of technical papers and finally a series of miners' circulars.

2. *The Platinum and Platiniferous deposits of the Ural.*—Prof. L. DUPARC has given (Arch. Sci. phys. nat., vol. xxxi) a full and valuable account of the deposits of platinum in the Ural, the single region upon which the world depends now for substantially all its supply of that metal. His researches on the subject have extended over a period of more than ten years. Briefly stated, he shows that the platinum is immediately associated with a band of basic eruptive rocks following more or less closely the watershed between Europe and Asia, particularly on the eastern side of the mountains. This band extends from the northern to the central Ural, while farther south it is continued by a series of isolated occurrences having the same general trend. In this, the western, zone occur the important deposits of platiniferous dunite. To the east lies a second band, shorter and not continuous, in which serpentine rocks prevail; just to the south of Ekaterinenburg it disappears or becomes lost in the first zone. These bands are flanked on both sides by metamorphic crystalline schists.

With respect to the individual occurrences, described in detail by the author, they show in general a mass of dunite at the center, more or less elliptical in form, with its axis approximately north and south. A border of more or less developed pyroxenite—also carrying platinum—is observed accompanied by certain melanocratic rocks and, in addition, an external zone of feldspathic rocks, including gabbros, diorites, etc.

The platinum occurs in the dunite both directly crystallized with the olivine and also with the chromic iron; in the latter case the platinum sometimes forms a spongy mass enclosing chromite grains. Both in the dunite and the pyroxenite the platinum is regarded as a magmatic mineral, a product of the differentiation of the magma. It is interesting to note that by careful search it has been found possible to observe the platinum in place in the dunite, although such an occurrence is rare.

The author has also earlier described (with P. Pamphil) the various peculiar types of rock associated with the platinum (koswite, issite, etc.) and has also (with H. C. Holtz) given analyses of many samples of the platinum.

3. *The Gabbros and Associated Rocks at Preston, Connecticut*; by G. F. LOUGHLIN, Bull. 492, U. S. Geol. Surv., 1912.—This bulletin describes an area of about one hundred square miles in eastern Connecticut. The bed rock formations comprise (1) Metamorphic sedimentary rocks—quartzite, quartz-biotite schist, hornblende schist, black pseudoporphyrific schist (Kinsigite), and dolomite; these are assigned provisionally to Cambrian and Carboniferous ages. (2) Gabbro—two principal and several minor varieties. (3) Granite—three varieties. The gabbro was the

first intrusive ; it preceded and was of sufficient mass to control the large regional metamorphism which followed. The secondary lines so developed determined the direction of the granite intrusion that accompanied the regional movement. The great Lantern Hill quartz is considered to have originated from a more or less complete replacement of alaskite by quartz during the pneumatolytic stage of granite intrusion. The bulletin as a whole is distinctly petrographic in character.

R. W.

4. *Dana's Manual of Mineralogy; for the Student of Elementary Mineralogy, the Mining Engineer, the Geologist, the Prospector, the Collector, etc.*; by WILLIAM E. FORD. New edition, entirely revised and rewritten. Pp. 480; with 357 text figures and 10 half-tone plates. 1912. New York (John Wiley & Sons) and London (Chapman & Hall).—Dana's Manual has played an important part in the elementary instruction in Mineralogy since its first publication in 1848. The work has been revised several times and in 1878 it was rewritten and an extended chapter on petrography added. A fourth edition, further revised, was issued in 1887, but though many times reprinted, twenty-five years have now passed since any change has been made in the text. There has been, therefore, a pressing call for the thorough working over of the volume, which has been ably accomplished by Professor Ford. In fact, the book as now issued is from beginning to end a new one although carried out on the same lines as its predecessors. The wide experience of the present author in teaching elementary classes in mineralogy has enabled him to present the whole subject in a thoroughly fresh, clear, and concise form.

Thus, starting from a book of well-recognized merits in its earliest forms, he has produced a work which should be widely useful not only in elementary instruction but also meet the needs of those interested in the science on the practical side.

In the arrangement of species, the chemical order has been followed instead of bringing the compounds of a given metal together as in earlier editions. But the end aimed at in that method has been accomplished by the addition of a chapter detailing for each metal the prominent species and giving the essential facts in regard to their occurrence as ores. The extensive chapter on "Rocks" of the two preceding editions has been omitted since several books on this special subject are now available; a brief chapter is included, however, giving the chief types of rocks and the minerals prominent in their formation.

The concluding section of the volume is given to a series of determinative tables based upon physical characters. In this the prominence of the individual species is indicated by the character of the type employed. In an appendix a summary is given of the mineral production for the United States in 1910; it is stated that these tables are to be revised from time to time so as to keep the information given as nearly as possible up to date.

The illustrations in the text are for the most part new, and a series of half-tone plates give reproductions of typical specimens.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *On a Period of 33.33 years in the Earth's Climate, and its connection with Sun Spots*; by JONAS ZILIUS. Reprinted from *Das Weltall*, the astronomical periodical of the Treptow Observatory. Pp. 10, 4to.—This is one of a series of papers on the subject of the periodicity of terrestrial phenomena in general and their connection with sun spots. Since Fabricius discovered sun spots in 1611 and the apothecary Schwab detected with his "imperturbable telescope" their periodicity in 1843, and Wolf in 1879 fixed the length of the period at 11 years, the idea of the influence of these solar disturbances on terrestrial affairs has continually grown until, in the investigations of Dr. Zilius, it has reached formidable proportions. How many new cases of this connection he has discovered and investigated does not appear from this article.

He presents tables of deficiency and excess of rainfall at Paris, Prague, Madras, and Bernaul from 1815 to 1884. The wettest and driest years do not fall exactly together at these stations, but they average up to show a maximum of dryness in 1833-4 and 1866-7.

These agree with minima of sun spots at 1833.3 and 1866.8, and these in turn coincide with the displays of the Leonids or November meteors.

One cannot but be impressed with the author's power of marshalling statistics, but there also comes to mind the saying that "figures cannot lie but they are prone to prevaricate." W. B.

2. *The Elements of Statistical Method*; by WILFORD I. KING, M.A., University of Wisconsin. Pp. xvi, 250. New York, 1912 (The Macmillan Company).—The author claims, and no doubt correctly, that no book published in America has attempted to cover the field of statistical method in its present state of advancement, while those published abroad are either partial or technical. This volume presents the subject simply and free from all intricate mathematical arguments. It is in form suitable for use as a text-book, but at the same time it is convenient and attractive for general reading.

W. B.

3. *Archiv für Zellforschung*, edited by Dr. RICHARD GOLDSCHMIDT, Professor in the University of Munich.—Part I of the eighth volume of this well-known journal, devoted to cytological investigation, is really a botanical number. In addition to fourteen brief reviews of recent botanical papers, it includes the following original contributions: Kernstudien an Pflanzen, by H. A. C. Müller; Etudes sur le développement du sac embryonnaire et sur la fécondation du *Gunnera macrophylla*, by J. A. Samuels; and Cell Structure, Growth, and Division in the Antheridia of *Polytrichum juniperinum*, by Charles E. Allen.

L. L. W.

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—♦♦—
ART. XXXI.—*On the Emission of Electrons by Metals under the Influence of Alpha Rays*; by H. A. BUMSTEAD and A. G. MCGOUGAN.

I

Introduction.

IN a previous paper under the same title by one of the present authors,* an account was given of some experiments upon the so-called δ -rays which are emitted by metals when struck by α -rays. The emission is known to consist of electrons moving with comparatively small velocities. Maximum estimates of their velocity, based upon the potential difference necessary to cause saturation of the current carried through a high vacuum by these electrons, give about $3 \times 10^8 \frac{\text{cm}}{\text{sec}}$, correspond-

ing to a potential difference of about 25 volts; minimum estimates, obtained by measuring the positive potential which a source of δ -rays will attain if insulated in a high vacuum, give velocities corresponding to 1 to 3 volts. Campbell† has recently brought forward some evidence for believing that the electrons have considerably smaller velocities even than this, if indeed they have any measurable velocity at all. The experiments to be described in § 3 of this paper, however, render this conclusion improbable.

In the previous paper it was shown that there was a close analogy between the emission of δ -electrons by a metal and the ionization of a gas by α -rays. The number of electrons emitted by the metal varies with the speed of the α -particles in the same manner as the number of ions produced in a gas; so that, by interposing various thicknesses of aluminium foil

* This Journal, xxxii, 403, 1911; Phil. Mag., xxii, 907, 1911.

† Phil. Mag., xxiii, 481, 1912.

between the source of α -rays and the metal, one can plot a curve entirely similar to the ionization curves first obtained by Bragg. The number of electrons emitted by the metal increases with the number of foils interposed until their combined thickness is nearly equal to the range of the α -rays in aluminium, after which the emission of electrons falls off rapidly.* The increase in the number of electrons with diminishing speed of the α -rays, however, is not so great as the increase in the number of ions in a gas. The ionization curve of the metal lies within, or to the left of, the corresponding curve for gaseous ionization and has a less pronounced maximum or "knee" just before the end of the range is reached. This result was anticipated before the experiments were undertaken, for reasons given in the previous paper. The same arguments which led to this conclusion also gave reason to believe that the curve for a metal of high atomic weight, such as gold, would lie within that of a metal of lower atomic weight, such as aluminium, just as the latter would lie within the curve of gaseous ionization. This expectation, however, was not fulfilled by the results of the experiments. The curves for gold and for aluminium coincided within the limits of accuracy of the somewhat rough method of determining them which was used.

Quite apart from the theoretical reasons discussed in the former paper, it was somewhat surprising to find that two metals which differ so much as aluminium and gold gave, nevertheless, the same ionization curves. For the ionization curves of gases and vapors differ considerably among themselves, not only in the area enclosed (total ionization) but also in their shape.† The close similarity between the curves for aluminium and gold gave rise to the suspicion that the electrons which had been producing the effects observed came not from the metals but perhaps from a layer of adsorbed gas which was the same in both cases. In order to test this possibility the following experiment was made.

§ 1. *Attempt to Remove Adsorbed Gases by Heating.*

A strip of thin platinum foil, 6^{cm} long, 3·7^{cm} wide, and $2\cdot4 \times 10^{-4}$ ^{cm} thick was stretched horizontally between two heavy brass clamps; the clamps were carried each on a vertical copper rod which passed through the cover plate of the evacuated chamber in which the δ -ray effects took place; the rods were insulated from the plate by ebonite, an earthed guard

* The increase in the emission as the speed of the α -particles decreases has also been observed by Campbell, *Phil. Mag.*, xxi, 276, 1911.

† Taylor, *Phil. Mag.*, xxi, pp. 578, 575, 1911.

tube, and amber, and the joints made tight with sealing wax. The platinum foil was arranged so that it could be exposed to a pencil of α -rays from polonium deposited on the end of a copper plug 4^{mm} in diameter. Between the polonium and the platinum, one could interpose aluminium foils, without interfering with the vacuum, in the manner described in the former paper. Two, three, four, five, or six layers of foil could be interposed, each 3.2×10^{-4} cm thick. The case was exhausted to about $.0001^{\text{mm}}$ with the help of charcoal and liquid air; one of the insulated copper rods which carried the platinum foil was connected with a quadrant electrometer, the case surrounding the exhausted chamber was charged positively, and measurements of the negative current leaving the platinum were taken in the usual manner. After an "ionization curve" had been determined in this way, the platinum strip could be heated by a current sent through it and the two copper rods, and the curve could be again determined, when the liberated gas had been removed.

Even before the platinum strip was heated its behavior gave evidence that the occluded gases had some effect upon the phenomena, if only a temporary one. With the metals used previously, the saturation value of the current had been obtained with + 40 volts on the case. With the platinum, an hour after the liquid air had been applied to the charcoal, it required + 160 volts to cause saturation and the current at this potential was 20 per cent greater than at 40 volts. Four hours later, 120 volts was sufficient to cause saturation, and the current was only 12 per cent greater than at 40 volts. After an interval of 24 hours, saturation was reached at 80 volts with a 5 per cent increase over 40 volts. During the same time the magnitude of the current (taken under similar conditions) fell off about 30 per cent. But the *shape* of the ionization curve, obtained by using a saturating potential and interposing aluminium foils, changed very little, if at all, while these very considerable changes were going on in the conditions of saturation and in the actual magnitude of the current. The results are given in Table 1. The first line of the table gives the time after the liquid air was applied to the charcoal bulb, the second line gives the value of the currents (with two foils interposed) corresponding to these times; the last five lines of the table give the values of the current when different numbers of foils are interposed, the current with two foils being taken as 100 in each case, to facilitate comparison.

It will be seen that the relative values for 2, 3, and 4 foils show no progressive change with the time; the differences between them are of the order of magnitude of the experimental errors. The values for 5 and 6 foils, however, appear

TABLE 1.

Time	1 hr.	2 hrs.	4 hrs.	6 hrs.	24 hrs.
C ₁	186	174	150	146.5	129
Foils					
2	100	100	100	100	100
3	112.0	111.2	112.3	113.0	111.8
4	103.8	103	105	103.3	104.7
5	59.5	60.3	64	63.7	66.2
6	23.1	23	25.3	25.6	26.6

to increase with the time; these values are on the decreasing portion of the ionization curve, where a small change in the range of the α -rays makes a large difference in the current. The observed increase can be explained by supposing that the progressive removal of occluded gas from the platinum foil slightly diminishes its stopping power for α -rays and thus the δ -radiation from the emergence side is increased.

After making the measurements which are recorded in the last column of Table 1, a current of 12 amperes was passed through the platinum foil. With this current a bright red heat was obtained in the middle of the foil, fading away gradually to the ends, which were cooled by conduction through the clamps and copper rods.* The current was continued for ten minutes, during which time the pressure rose from less than $\cdot 0001^{\text{mm}}$ to $\cdot 004^{\text{mm}}$. The charcoal bulb did not absorb the gas, although the liquid air was left on over night; this is doubtless due to the fact that the gas emitted by the platinum contained considerable hydrogen which is not readily absorbed by the charcoal. The liquid air was then removed, and the Toepler pump was operated, while the charcoal was re-heated to aid in sweeping out the hydrogen. When a pressure of about $\cdot 001^{\text{mm}}$ had been reached the liquid air was again applied, and the pressure soon fell to less than $\cdot 0001^{\text{mm}}$. After two hours the value of C₁ was 134 and the variation for the different foils interposed did not differ appreciably from the last column of Table 1.

This test, however, was not very satisfactory on account of the failure of the charcoal to remove promptly the gas emitted by the heated platinum. Accordingly the charcoal bulb was removed and a Gaede pump substituted for the Toepler pump. When a vacuum of $\cdot 0001^{\text{mm}}$ had been maintained for an hour,

* A glass window in the brass case permitted observation of the foil.

measurements were taken as before. Then the strip was heated five times, for ten minutes at a time, with intervals of fifteen minutes between, to avoid too great heating of the clamps and copper rods; the pump was kept running continuously. Measurements of the δ -ray current were then made as before. The results are given in Table 2.

TABLE 2.

	Before	After
Foils	$C_2 = 150$	$C_2 = 184$
2	100	100
3	110	108.2
4	102.7	101.0
5	62.5	61.0
6	24.7	24.2

Here there does appear to be a slight alteration in the form of the ionization curve, and in the direction expected. But the differences are so slight that no great confidence can be placed in the result. Further experience with the method did not give any reason for hoping that the question as to the effect of adsorbed gases could be definitely settled in this way.

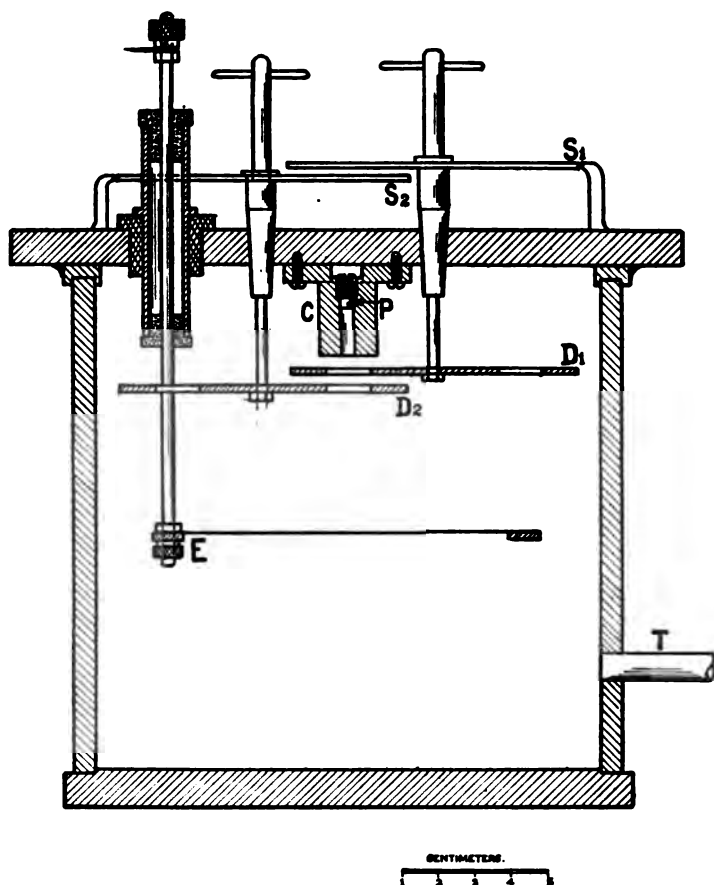
The results of this experiment are susceptible of two quite different interpretations. We may say that, since the heating of the platinum strip did not alter the shape of its ionization curve, we may conclude that this shape is due to the properties of the metal itself and not to adsorbed or occluded gases. On the other hand, we may put the emphasis on the fact that, under certain conditions, at least 30 per cent of the δ -ray effect is due to such gases, and that when these are removed there is no change in the shape of the curve. If the residual effect is really due to the metal we must suppose that platinum and the adsorbed gases have ionization curves of very nearly the same shape, which is not altogether probable considering the variations which are met with in the curves of gaseous ionization. From this point of view, therefore, it seems more probable that the δ -ray emission (slow electrons) is mainly due to such a layer of gas, which may be reduced but not entirely removed by the methods which we have employed.*

* Since the present investigation was completed, a paper has appeared (Pound, Phil. Mag., xxiii, 813, May, 1912) in which the effect of occluded gases upon the magnitude of the δ -radiation is clearly brought out.

§ 2. *Determination of the Ionization Curves of Various Metals.*

In the determination of the ionization curve of platinum in the preceding section and of those of gold and aluminium in the previous paper, the metals were so thin that the α -rays passed through them, except when they were near the end of their range. This has the advantage that, at least until the

FIG. 1.



top of the curve is reached, no correction for the charge of the α -rays is necessary and one need not apply a magnetic field in order to determine this charge. On the other hand, a difficulty results if one wishes to make a careful comparison of different metals. It is impossible to obtain foils of different metals

which have the same retarding effect on the α -rays; and hence the *emergence* δ -radiation from the different metals correspond to different speeds of the α -rays even when the same number of aluminium foils are interposed. This is plainly shown by a comparison of the results for platinum with those for gold and aluminium given in the previous paper. The platinum foil is so much thicker than the others that the entire form of the curve is distorted. Moreover, in the foregoing experiments, very few points on the curve were taken, so that, indeed, it is only by courtesy that it can be called a curve at all. For these reasons a much more careful determination was undertaken by means of the apparatus shown in fig. 1.

A copper plug, P, 4^{mm} in diameter, whose lower surface is covered with polonium, is surrounded by a brass cylinder, C, which limits the cone of the rays so that they fall completely within the brass ring, E, which supports the sheet of metal under investigation. In order to obtain more points upon the ionization curves, two discs, D₁ and D₂, are used instead of the one which was used in the previous experiments. In order to make the drawing clearer, the rod supporting E is shown in the same plane with the axes of the discs; in the actual apparatus it is in the plane perpendicular to this. The discs are divided into eight equal sectors. D₁ has a hole 1.5^{cm} in diameter cut in each sector. One hole is left open and the others are covered with 1, 2, 3, 4, 5, 6 and 7 layers of aluminium foil of thickness 3.2×10^{-4} cm, having a retarding effect upon the α -rays, according to Taylor's results, equivalent to that of 0.58^{cm} of air (air equivalent). The disc D₂ has one sector without a hole so that the α -rays can be stopped completely; the other sectors have holes, one of which is left open, others being covered with 1, 2, 3, and 4 layers of thinner aluminium foil, 0.64×10^{-4} cm thick. Thus five of the thin foils are equivalent to one of the thicker. The dials, S₁ and S₂, outside the evacuated chamber enable one to set the discs D₁ and D₂, so that any combination of the thick and thin foils may be interposed in the path of the α -rays, or the brass sector may stop them entirely, or the two holes allow them an uninterrupted passage to the electrode.

The metal plate attached to the ring, E, was in every case chosen of sufficient thickness to absorb completely the α -rays so that the δ -electrons were emitted only from the side on which the α -rays were incident. The electrode is insulated from the case by amber, guard-tube and ebonite, and is connected to a sensitive gold leaf electroscope of the Hankel type.* A key is connected to a potentiometer arrangement so that

* This instrument is described in the previous paper, this Journal, xxxii, 405, 1911; Phil. Mag., xxii, 909, 1911.

the leaf can be insulated, grounded, or charged to any desired potential; the volt-sensitiveness was thus taken after each reading. In the following measurements, the sensitiveness was adjusted to give a deflection of about 25 divisions on the scale of the microscope for 0.2 volts. The tube T is connected to pump, gauge, and charcoal bulb.

When the α -rays fall on the electrode, E, they carry over to it their positive charges; the δ -rays which they excite are negatively charged and these, leaving the electrode, add to its positive charge. In order to insure the removal of all the emitted electrons from the electrode and to prevent the δ -rays emitted by other parts of the apparatus from reaching it, a positive potential of 40 volts is applied to the case. If a sufficient magnetic field is applied with its lines of force parallel to the electrode, the electrons emitted will be turned back to the electrode, and in this way the charge due to the α -rays alone may be determined. For this purpose an electromagnet was constructed of Swedish iron, 2 inches square in section. It was forged into the shape of a rectangle 30^{cm} by 25^{cm} and a gap left in one side 15.2^{cm} long which was just sufficient to embrace the exhausted chamber. It was wound with about 1000 turns of No. 14 cotton-insulated, paraffined wire. The field at various points between the poles was measured with a Grassot flux-meter; a current of 5 amperes produced a field, midway between the poles, of 95 gauss. It was found that, with the case earthed, this field reduced the current received by the electrode to a minimum; no further diminution occurred when the current through the magnet-coil was increased to 9 amperes. On account of the large air-gap the field was very nearly proportional to the current.

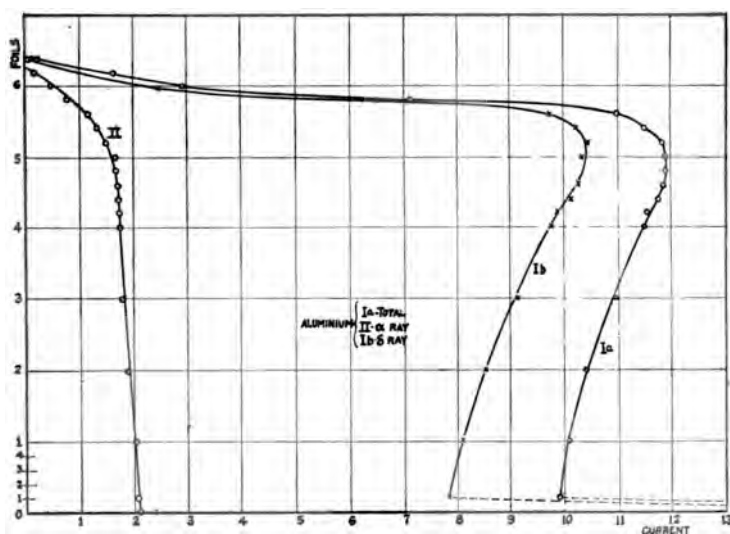
The results obtained when the electrode was a sheet of aluminium are shown in fig. 2, in which the ordinates represent the number of aluminium foils between the polonium and the electrode, and the abscissæ are the currents measured by the electroscope. Curve Ia gives the results with no magnetic field, and thus represents the total effect due to both α - and δ -rays. Curve II shows the currents observed when the magnetic field was on, due to the charge carried by the α -rays alone. Curve Ib is obtained by subtracting the abscissæ of II from Ia and represents the δ -ray effect, or "ionization" of the metal.

It will be observed from an inspection of Curve II that the number of α -particles which reach the electrode apparently decreases as more foils are interposed. Up to five thick foils this decrease is approximately linear, and amounts to about 20 per cent of the total. This is too great a falling off to be attributed to the scattering of the α -rays according to the

results obtained by Geiger.* It is possible that an explanation of this effect may be found in the phenomena to be discussed in the following section. Beyond five thick foils, the number of α -particles diminishes rapidly; this is doubtless due to their absorption in the aluminium foils, the more oblique rays being the first to be stopped.

By dividing the abscissæ of Ib by those of II, a curve could be obtained which would represent the ionization or δ -ray

FIG. 2.



effect produced by a fixed number of α -particles, which is, strictly speaking, what should be given by an ionization curve. Nevertheless, it does not seem advisable to use results thus obtained in the present investigation; the α -ray currents are small and the errors introduced by using them as factors might be considerable. Moreover our purpose is primarily to compare the effects with different metals. The ionization curves of gases and vapors have also usually been obtained without allowance for the decrease in the number of α -particles, so that a more direct comparison with them is possible by using the curve Ib. An estimate of the number of δ -electrons due to one α -particle may be obtained, however, by dividing the abscissæ of Ib by those of II. Allowing for the fact that the charge on an α -particle is twice the electronic charge, we find that the number of δ -electrons per α -particle emitted by an

* Proc. Roy. Soc., lxxxiii, 492, 1910.

aluminium plate from the incidence side only, varies from 7 to 17 as the speed of the α -rays is gradually reduced.

One very striking result appeared in the course of these experiments which was quite unexpected from anything previously known as to the effects of α -rays. As the number of aluminium foils is decreased, the ionization follows a perfectly regular Bragg curve until only one thin foil is left. When, however, this is removed so that there is no obstacle between the polonium and the electrode, a very large increase is observed in the δ -ray current. Thus in the series represented by fig. 2, the δ -ray current for one thin foil is 7.82 while for no foils it is 16.27, an increase of 107 per cent. It has been shown that this is due to a very absorbable radiation consisting partly of electrons moving with considerably higher velocities than the hitherto recognized δ -rays. An investigation of this absorbable radiation will be described in the next section.

Experiments similar to those which have been described at length in the case of aluminium were made also with copper, gold, lead, and platinum. In all cases the surfaces of the metals were made clean and bright by fine sandpaper. The magnitude of the δ -ray currents obtained from the various metals under similar conditions were not very different from each other, when correction was made for the decay of the polonium in the intervals between the experiments. The main purpose of the present investigation was to ascertain the variations in the *form* of the ionization curves for different metals and not their absolute magnitudes; for this reason no attempt was made to get an accurate determination as to the latter point. It is rendered difficult by the fact, discussed in §1, that the δ -ray current falls off with the lapse of time after the liquid air has been applied to the charcoal. This effect was observed in all the metals studied, but it was not quite so marked as in the case of the thin platinum foil described in §1. However, the diminution in the current sometimes amounted to as much as 20 per cent and continued to be noticeable for two or three days.* As in the case of the platinum foil, the relative values at different points of the range of the α -particles were not affected by this variation, the ratio of the ionizations at any two points remaining practically constant.

The results for the different metals are given in Table III and plotted in fig. 3. The values used are the currents due to the δ -electrons alone, corresponding to Curve Ib in fig. 2. In order to make the comparison easier they have been reduced to the same scale by making the current for one thick foil the

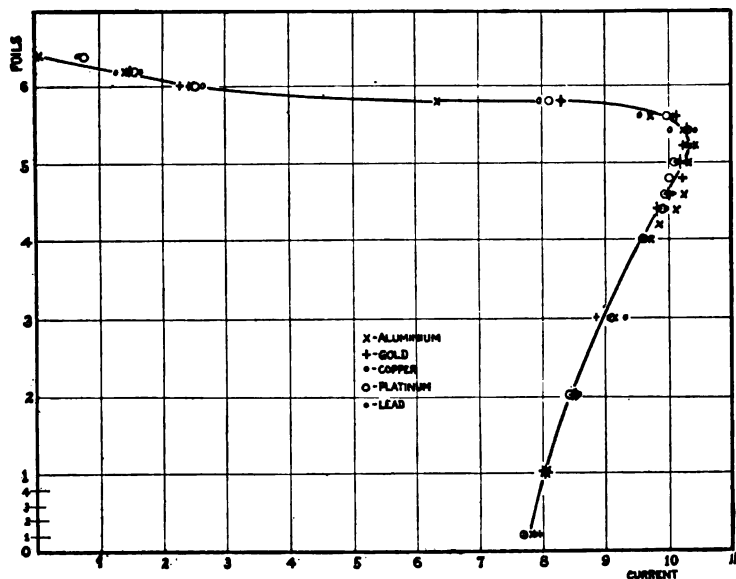
* Our observations in regard to the variations in the magnitude of the δ -ray current with different metals is in substantial agreement with those of Campbell, Phil. Mag., xxi, 298, 1911.

same for all the metals ; the other currents are then altered in the same ratio.

TABLE III.

Al. Foils		Al	Cu	Au	Pb	Pt
Thick	Thin					
0	0	16.27	14.67	15.47	13.57	15.87
0	1	7.82	7.72	7.92	7.87	7.72
1	0	8.07	8.07	8.07	8.07	8.07
2	0	8.53	8.58	8.43	8.53	8.41
3	0	9.17	9.02	8.82	9.32	9.08
4	0	9.77	9.67	9.62	9.57	9.60
4	1	9.83	9.82			
4	2	10.12	9.92	9.82	9.85	9.90
4	3	10.24	9.99	9.99	10.04	9.94
4	4			10.05		10.00
5	0	10.31	10.16	10.19	10.26	10.11
5	1	10.45	10.25	10.25	10.35	10.25
5	2	10.21	10.00	10.31	10.41	10.26
5	3	9.71	9.56	10.11	10.06	9.96
5	4	6.35	7.95	8.30	8.30	8.15
6	0	2.45	2.65	2.29	2.41	2.51
6	1	1.43	1.73	1.56	1.25	1.61
6	2	.14	.77	.06	.73	.83

FIG. 3.



The points for the different metals lie so closely together that only one curve has been drawn. Anyone who has had experience with such measurements will recognize that the differences are too small to have any significance. Even in the case of aluminium, which appears to differ somewhat from the others, the differences are not at least more than 2, or 3 per cent; and differences of this order, which are obviously accidental, occur in all the curves. We are forced to conclude, therefore, that the ionization curves as observed, for all metals, have the same form. This is in agreement with the results of the less accurate experiments upon gold and aluminium described in the previous paper. Whether or not the curves so obtained really represent the ionization of the metals is by no means certain. As has been said, the fact that there is no change in the form of the curve, when its magnitude is considerably decreased by the removal of a surface film of gas from the metal, makes it not improbable that the whole effect may be due to such a film. The probability of this explanation is increased by the fact that the ionization curves of gases and vapors do vary considerably; and it seems, therefore, unlikely that metals, so different in all their properties as those used above, should show such complete similarity in this respect.

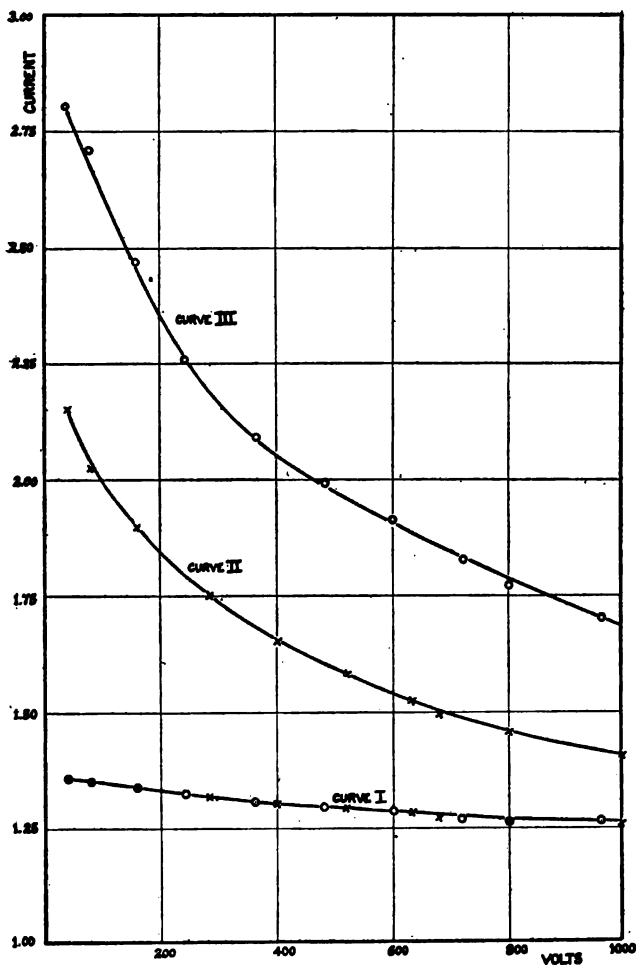
§ 3. *Investigation of an Absorbable Radiation accompanying Alpha Rays.*

When the last thin aluminium foil is removed from the path of the α -rays the number of electrons leaving the metal plate is greatly increased; this is shown by the first line of Table III, § 2. There appears to be, therefore, a very absorbable or "soft" radiation emitted by the polonium, which is completely stopped by 0.64×10^{-4} cm of aluminium. To obtain an idea of the nature of this radiation some experiments were made, in which we used the apparatus described in the previous paper.* It is substantially the same as that shown in fig. 1 of the last section, except for slight differences in dimensions, and the fact that there is only one disc to carry the aluminium foils instead of two. A much stronger preparation of polonium, which we owe to the kindness of Professor Boltwood, permitted the use of an electrometer instead of an electroscope. A brass plate was used as the source of δ -rays, and the negative current from it was measured, with one thin foil interposed and with none, when various positive potentials were applied to the case ranging from 40 to 1000 volts. The results of these measurements are shown in fig. 4, where the abscissæ are the potentials ap-

* Phil. Mag., xxii, 917, 1911; this Journal, xxxii, 413, 1911.

plied to the case and the ordinates of Curves I and III are, respectively, the currents observed with one foil, and with no foils, interposed. The difference between the ordinates of the two curves shows the effect of the assumed soft radiation. This

FIG. 4.



effect is greatly diminished as higher positive potentials are applied to the case, so that at 1000 volts it is reduced to about one-fourth of its value at 40 volts. This indicates that the radiation consists of electrons with much higher velocities than those attributed to the δ -rays, and with a wide range of

velocities. As the positive potential on the case is increased, more and more of these electrons are withheld from reaching the brass plate. The fact that this radiation communicates a positive charge to the plate is not an obstacle to the hypothesis that it consists of electrons. Since the early experiments of Lenard it has been known that electrons, moving with velocities corresponding to several hundred volts, when they fall upon a metal, cause the latter to emit secondary electrons, which may carry a larger negative charge away from the metal than it receives from the incident stream.*

It seemed possible that the diminution in the current with an increasing field might be due to an effect upon the electrons emitted by the plate rather than upon the radiation itself—for example, by increasing the reflection, or the number of secondary electrons from the case. In order to test this possibility the brass plate (corresponding to E in fig. 3) was enclosed in a tin box, whose top was made of wire gauze in order to permit the α -rays and the new radiation to reach the plate. It was insulated from the case and could be charged by means of an external electrode. The box was kept charged to 40 volts, while positive potentials up to 1000 volts were applied to the case; in this way the field in the vicinity of the plate, E, remained practically constant while the soft radiation had to pass through a variable field. The results were not essentially different from those shown in fig. 4.

In order to determine whether or not this soft radiation was peculiar to polonium, experiments were made in which the active deposit of thorium (obtained from a preparation of mesothorium) was used. It was much less active than the polonium and more time was necessary for each reading; on account of the decay of the activity it was not practicable to wait until the changes due to the removal of the gas layer had ceased, before beginning the readings. It was thus impossible to obtain as satisfactory numerical results as with the polonium, but there could be no doubt about the existence of the soft radiation. It produced a greater effect, in proportion to that due to the α -rays, than in the case of polonium; the ratio was about twice as great. On the other hand, the diminution produced by an opposing electrical field was not as great as with the polonium; with 940 volts on the case, the effect of the soft radiation was about one-half as great as with 80 volts. A similar change of potential with the polonium reduced the effect to one-third.

* See also Gehrts (Ann. d. Phys., xxxvi, 1001, 1911), where it is shown that, when electrons with a velocity corresponding to 200 volts fall upon a copper plate, the secondary electrons carry away from the plate more than twice the charge brought to it by the incident electrons.

Returning to fig. 4, it will be observed that Curve I, which was supposed to be due to the α -rays alone, shows a diminution of the current as the potential on the case is increased, which is similar to that of Curve III but much less in amount. This was at first difficult to explain; it is quite evident that the fields used were too small to accelerate the α -rays sufficiently to cause an appreciable decrease in the δ -ray current. The fact that the soft radiation accompanied the α -rays in the thorium deposit as well as in the polonium suggested that it might be a secondary effect; if this were so, then the currents plotted in Curve I (fig. 4) would be due not to the α -rays alone, but there would be a small admixture of the assumed secondary rays from the lower side of the aluminium foil on the disc.*

A small circle of the thicker aluminium foil, of the same diameter as the opening in the brass cylinder, C (fig. 1), was pushed up against the polonium. In this way any soft radiation coming directly from the polonium would be stopped; but a secondary radiation due to the impact of the α -particles on the inner walls of the brass cylinder, C, would not be stopped unless a foil were interposed below the cylinder by means of the wheel. The experiment was made as before by applying various positive potentials to the case and taking alternate readings with and without the foil below the cylinder.

The results are shown in Curve II of fig. 4. The sensitiveness of the electrometer had changed by about 5 per cent since the experiments with the uncovered polonium; the values of all the currents were reduced in the same ratio so that the measurements *with* the interposed foil should agree. In Curve I, the crosses represent the measurements when the polonium was covered, the circles those obtained when it was not covered, a thin foil being between the cylinder and electrode in both cases. A comparison of Curves III and II shows that the direct radiation contains a component which is much less affected by the retarding field than the secondary radiation alone. This agrees with the results of Wertenstein (l. c.), who, however, worked with a magnetic instead of an electric field. If we assume that the soft radiation is made up of two portions, one coming directly from the polonium, and not retarded by the field, while the other is secondary and consists of electrons, we may show by a simple calculation that the experimental results are accounted for in a very satisfactory manner.

* At this stage of our experiments the very interesting paper of Wertenstein (*Le Radium*, ix, p. 6, 1912) came to hand. By measuring the ionization due to Ra C in gases at low pressures, he has demonstrated the existence of two soft radiations: one is secondary, and deviable in a magnetic field, and doubtless consists of electrons, while the other is not appreciably deflected in a magnetic field of 1100 units. The remainder of our work was done with a knowledge of Wertenstein's results, and the next experiment was directly suggested by his paper.

Let a be the current of δ -electrons leaving the electrode due to the pencil of α -rays which strike it; this is present in all the curves. Let b be the current due to a soft radiation from the polonium which is unaffected by the field; this is present in III but absent in I and II. Let s be the current due to a secondary radiation (consisting of electrons) when there is no obstacle between the polonium and the electrode (Curve III); this will vary with the electric field. The secondary radiation which produces s is due to nearly all the α -particles liberated by the polonium, through the complete solid angle, 4π , but the secondary rays from the plug which carries the polonium and from the deeper parts of the cylinder are cut down by the limited aperture. When the polonium is covered, the secondary rays are due to the α -particles which emerge through a solid angle approximately equal to 2π ; their effect will be equal to ms where $m < 1$. (Curve II.) Finally when the thin foil is interposed below the cylinder, the secondary rays from the lower side of the foil will be due to the α -rays which get out of the cylinder and pass through the foil; the solid angle in this case is about 0.14π , but the beam of secondary rays is not limited by any diaphragm. We may write ns , ($n < m$) for the δ -ray current produced in this case (Curve I).

If, then, y , y_1 , and y_2 are respectively the ordinates of Curves I, II and III, we have,

$$\begin{aligned} y_2 &= a + b + s \\ y_1 &= a + ms \\ y &= a + ns \end{aligned} \quad (1)$$

where a , b , m , n are constants and s varies with the potential applied to the case. From these we obtain

$$(y_2 - y_1) = b + \frac{1-m}{m-n}(y_1 - y);$$

by plotting $(y_2 - y_1)$ against $(y_1 - y)$ from the curves in fig. 4, and drawing a straight line to represent the points as well as possible, we obtain,

$$b = 0.20; \quad \frac{1-m}{m-n} = 0.62$$

From an extension to 1700 volts of Curves I and II which was made later, we get as an approximate value of $\frac{n}{m}$, 0.15. This makes $m = 0.65$; $n = 0.10$.

With these values we may calculate s for different values of the potential on the case, from the curves, by the equations

$$s = \frac{y_2 - y_1}{m - n}; \quad s = \frac{y_1 - y}{1 - m}$$

The values of s given in the second column of Table IV are means of the two values thus obtained.

TABLE IV.

$$a=1.24 \quad b=0.20 \quad m=0.65 \quad n=0.10.$$

Volts	s	y_1		y_2		y_3	
		obs.	calc.	obs.	calc.	obs.	calc.
40	1.39	2.82	2.83	2.15	2.14	1.36	1.38
100	1.20	2.63	2.64	2.00	2.02	1.35	1.36
200	0.90	2.35	2.34	1.85	1.82	1.33	1.33
300	0.71	2.16	2.15	1.74	1.70	1.31	1.31
400	0.60	2.05	2.04	1.65	1.63	1.30	1.30
500	0.54	1.98	1.98	1.59	1.59	1.29	1.29
600	0.48	1.91	1.92	1.54	1.55	1.28	1.29
700	0.41	1.85	1.85	1.50	1.51	1.28	1.28
800	0.34	1.78	1.78	1.46	1.46	1.27	1.27
900	0.29	1.73	1.73	1.43	1.43	1.27	1.27
1000	0.25	1.68	1.69	1.41	1.40	1.26	1.26

In this table the columns under "observed" are taken from the experimental curves; the columns under "calculated" are obtained from equation (1) with values of the constants given, and the values of s contained in the same line of the table. It is obvious that the relation between the three curves corresponds very closely to the hypothesis that, in addition to α -rays, a radioactive body emits a very absorbable primary radiation and that a secondary radiation consisting of moderately swift electrons is emitted by the source and also by any object which is struck by the α -rays.

This conclusion is in accord with the results of Wertenstein, who measured the ionization produced in air at low pressures by the radiations from Ra C, when the distance between the source and the ionization chamber was varied. He attributes the soft primary radiation to the recoil atoms of Ra D, and it seems very probable that this view is correct. His results differ from ours, however, in the relative magnitudes of the effects of the different types of rays. Thus he states (l. c., page 19) that, in a narrow ionization chamber and with a clean active surface, the soft primary rays (recoil atoms) may make five times as many ions as the α -rays. In our experiments the current of δ -electrons produced by the soft primary radiation is only $1/6$ of that produced by the α -rays. This discrepancy is due, at least in part, to the fact that the deposit of polonium which we used could not be regarded as "thin" in regard to

this very absorbable radiation. Wertenstein found that this radiation could be considerably increased by depositing the Ra C upon a platinum plate, and thus avoiding a film of oxide which formed on other metals under the action of the radium emanation. Another cause for the difference is probably to be found in the fact that his experiments were made at pressures of from 3 to 10^{mm} instead of in a high vacuum; in the latter case, fewer of the recoil atoms are charged and their ionizing effect might be expected to be less.

On the other hand, the ionizing effect of the secondary rays in his experiments was small, amounting only to about $1/5$ of the α -ray effect, whereas our results show that it causes the emission of 1.12 times as many δ -electrons as the α -rays. It is true that these results depend upon the dimensions of the cylinders which are used to limit the pencil of α -rays, but it seems scarcely possible that so large a discrepancy can be attributed to this cause. It may be that the secondary rays are more efficient in causing the liberation of δ -electrons from the metals than in ionizing a gas; it may be also that the transverse magnetic field used by Wertenstein to deflect these rays from his ionization chamber was not altogether effective in the presence of air which was necessary for ionization measurements.

The values of s in the second column of Table IV give some idea of the distribution of velocities among the secondary electrons, but no numerical results can be conveniently deduced from them. The number of secondary (in this case tertiary) electrons emitted by a metal when struck by a moving electron changes rapidly with the speed of the moving electron especially within the range of velocities with which we have to do in this case.* It will probably not be difficult, however, to determine the velocity distribution by using a Faraday cylinder as the recipient of the rays.

It is evident that the range of velocities extends from less than $3.8 \times 10^8 \frac{\text{cm.}}{\text{sec.}}$, which corresponds to 40 volts, to more than 18.8×10^8 , which corresponds to 1000 volts. An experiment, not here reported in detail, showed that there was still a very appreciable effect from the secondary radiation with an opposing potential of 1700 volts; this corresponds to a velocity of 24.4×10^8 . This is not far from the maximum estimate which Wertenstein obtained with the magnetic field, viz. 2.3×10^9 .

It is plain that the existence of this radiation vitiates the estimates which have hitherto been made of the velocities of the slow δ -electrons. Thus, for example, an insulated source of α - and δ -rays, within an earthed enclosure, will lose more

* See Gehrts, *Ann. d. Phys.*, xxxvi, pp. 1008 et seq., 1911.

swift electrons than it gains from the enclosure; its potential will rise until it can attract enough slow electrons to balance this loss. The value of this steady potential will not depend on the speed of the slow electrons so much as upon the size and shape of the enclosure in relation to the insulated source. If, as in Campbell's experiment,* the apparatus is arranged so that all the electrons from either of two electrodes A and B strike the other one, there is still a complication which renders impossible any simple interpretation of the results. Comparatively slight changes† in the velocity of the swift secondary electrons from A, for example, may alter considerably the number of slow tertiary electrons emitted by B. Thus false balances may be obtained which have little relation to the speed of the slow electrons. In fact it seems possible that the difficulties, which Campbell encountered when one of his electrodes was covered with soot,‡ and which led him to adopt the hypothesis that the δ -electrons had no appreciable velocity, may be accounted for in this way.

When a metal is struck by α -rays it is evident that some, at least, of the slow δ -electrons which result are not due to the direct action of the α -rays, but are produced through the intermediary of the swifter secondary electrons generated in the metal itself near its surface. The question naturally arises whether the whole of the effect may not be produced in this indirect way. A consideration of the results exhibited in curve I of fig. 4 shows that this is not beyond the bounds of possibility. In this experiment we have secondary rays produced by the same pencil of α -rays at two places,—the aluminium foil on the wheel and the plate corresponding to E, fig. 1. The δ -ray current from the plate due to the α -rays is 1.24; let us assume that it is produced as indicated above. The current produced by the secondary rays from the foil (with 40 volts on the case) is $ns = 0.14$; the ratio of these currents is 0.11. Now the plate subtends at the foil a solid angle of $4\pi \times 0.158$; for an electron generated in the place itself we may take the solid angle as 4π . Taking the figures as they stand, this would indicate that at least 11/15 of the supposed α -ray effect is produced indirectly by means of the secondary electrons generated in the plate. We may suppose that they give rise to the slow electrons, either as they emerge from the plate itself, or as they pass through the layer of gas which we have been led to postulate by the results of the preceding section.

If this should prove to be the mechanism of the emission of δ -rays by metals, it will at least render it probable that a simi-

* Phil. Mag., xxi, 280, 1911.

† See Gehrts, l. c.

‡ Phil. Mag., xxiii, pp. 54 et seq., 1912.

§ The dimensions are different from those shown in fig. 1.

lar process takes place when gases are ionized by α -rays. The column of ions following the track of the α -particle, which was assumed by Moulin, and which has recently been made visible in the beautiful experiments of C. T. R. Wilson, would then be made up of the tracks of many secondary electrons, radiating irregularly from the axis of the column, and extending only a small fraction of a millimeter from it.

Summary.

1. The number of δ -electrons emitted by a metal when struck by α -rays varies with the speed of the α -rays in the same manner as does the number of ions produced in a gas. Curves which represent this variation are similar in form to the Bragg ionization curve.

2. Such curves have been determined for aluminium, copper, gold, lead and platinum. Within the limits of accuracy of the experiments they have the same form for all these metals; this agreement is in contrast with the fact that ionization curves for different gases and vapors show marked differences in form.

3. The magnitude of the δ -ray effect, and the field necessary to cause saturation, decrease progressively for some time after the vacuum is produced. This is ascribed to the gradual removal of a layer of adsorbed gas; during this process the *form* of the "ionization curve" does not change. This suggests that the whole effect may be due such a layer which can not be entirely removed; the similarity of the curves obtained with different metals would thus find a natural explanation. However, an experiment, in which a strip of platinum was heated to red heat in a high vacuum, failed to give evidence of the removal of this assumed film.

4. Polonium and the active deposit of thorium emit a radiation which is completely absorbed by 0.64×10^{-4} cm of aluminium. This radiation causes the emission of electrons from metals which it strikes. It consists of two portions, one of which is primary and not appreciably affected by an electric field; the other is secondary and consists of electrons whose velocities range from less than 3.8×10^8 to more than 24.4×10^8 cm/sec. Wertenstein has found that Ra C emits similar soft radiations, which ionize a gas; he attributes the primary radiation to the recoil atoms.

5. The secondary radiation is emitted not only by the source, but by any object on which α -rays are incident. The electrons of which it consists have considerably higher velocities than the δ -rays hitherto recognized.

6. A part, at least, of the ordinary δ -radiation is due, not to the direct action of the α -rays, but to these secondary rays. So far as can be concluded from the present experiments, it is quite possible that the whole of the δ -ray effect may be thus produced.

ART. XXXII.—*The Flashing Arcs: A Volcanic Phenomenon*; by FRANK A. PERRET.

ON the afternoon of April 7, 1906, the present writer, in company with Professor Matteucci, was skirting the southern flank of Vesuvius on a trip to the main source of the lava at the Bosco Cognoli. The volcano at this time was entering one of those paroxysmal phases by which the eruption—already three days old—worked progressively up to its great culmination, which occurred, it will be remembered, between this and the following day. The ejected detritus was of a mixed nature, viz., the fresh lava, clear red in full daylight, being mingled with old material from the upper portions of the cone, then in process of rapid demolition. The frequency of the explosions varied from approximately one every three or four seconds to at least three per second. Although powerful, they were very sharp and sudden in their nature, and at the instant of each—but before it could be sensed by the eye or ear—a thin, luminous arc flashed upward and outward from the crater and disappeared in space. Then came the sound of the explosion and the projection of gas and detritus above the lip of the crater. The motion of translation of the arcs, while very rapid in comparison with that of the detritus, was not above the limits of easy observation and there could be no doubt as to the reality of the phenomenon, which was repeated some hundreds of times.

The writer attempted photography but without success, the failure being due in part, perhaps, to the velocity of the arcs and their very moderate brightness, but also most certainly to the extreme unlikelihood of the shutter being snapped at the precise instant of the apparition. One of the photographs is reproduced in fig. 1, and I have permitted myself to trace upon the negative film with aniline two circles which print out in the approximate appearance of the arcs, assuming these to have been arrested instantaneously during their up- and out-springing from the crater.* It should be stated that this illustration, because of its crudeness and the lack of motion, conveys but a poor idea of the actual phenomenon, the beauty of which lies in the delicate luminosity, the elegance and perfection of form, and the grace and vivacity of the arcs amid the contrasting color and relatively sluggish movement of their surroundings.

During the extraordinary activity of Stromboli in 1907 the writer did not observe the flashing arcs although some of the explosions appeared to have the qualities which should have

* It may be that I have centered the circles too high above the crater.

produced them, but the place of observation was probably too near the crater. The small eruption of Etna in 1908 was not observed, but the conditions were not, in my opinion, such as to have reproduced the phenomenon. At Teneriffe in 1909, although incandescent lava was still available for research work upon my arrival, the explosive effects, which had been powerful, were virtually at an end, and it was therefore with the greatest delight that during the 1910 eruption of Etna I again observed the flashing arcs.

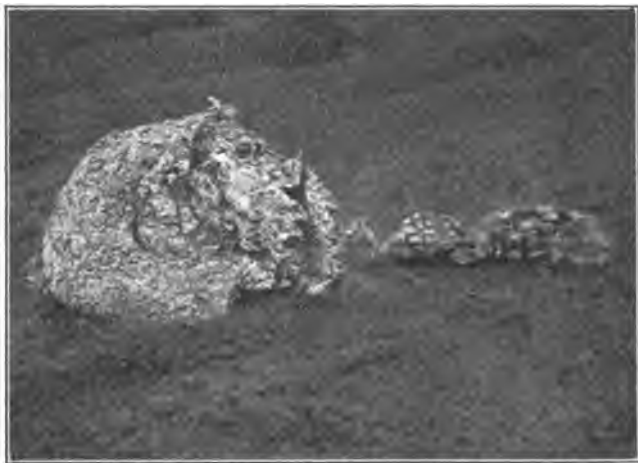
FIG. 1.



By a rare good fortune the explosions in this case were almost without detritus, thus forming a condition the very opposite to that at Vesuvius in 1906. It will be remembered that this eruption of Etna produced a fissure 2^{km} in length over which were formed some twenty-four small craters. The explosive forces were thus so subdivided and distributed that no very large cones of scorix were built up, many of the craters being little more than holes in the ground. One of these,

although larger than the average, was so perfectly free from surrounding débris that a post-eruption visitor might well have been pardoned for considering it the least important of the entire series. It was, however, the seat of all the heavier explosions, each of which hurled one or two bombs of stiff, incandescent lava to a considerable distance, but without any accompaniment of ash or other detritus. On the morning of March 30 bombs as large as a meter in diameter were ejected (fig. 2), and these explosions produced the flashing arcs which

FIG. 2.



were in all respects identical with those at Vesuvius. Until they were pointed out to him my guide did not observe them, and it is quite possible that I myself might not have seen them had I not known what to look for, as the absence of a darker setting and the lesser distance of the viewpoint rendered them more difficult of observation than at Vesuvius. Some fifteen were clearly seen by both of us, all the stronger explosions producing them.

What is the nature of this phenomenon? The only hypothesis which seems in accord with the observed characteristics sets forth a proposition which, at first thought, may seem almost startling, viz., that we have to do with *visible sound waves*. According to some far from accurate measurements made on the spot the velocity of propagation of the arcs *seemed* to correspond with that of sound. We may certainly assume the outburst to be spherical or at all events globular, as though a huge soap bubble were rapidly blown from the

crater and that the edge alone is visible and therefore appears from any point of view as an arc. The movement of this visible portion will therefore be at right angles to the line of sight and the arrival of the sound—from the crater radially to the observer—must be compared with the arrival of the arc at some point equidistant from the crater but at right angles to this radius. As the arcs rapidly fade into invisibility with increasing distance from their source the difficulty of accurate measurement will seem to be very great.

But if we attack the problem by the way of exclusion we shall find, I believe, that the velocity—even assigning to it values having a considerable margin above or below that of sound—can be made to harmonize with no other mode of motion. Actual mass movement, *i. e.*, motion of translation of any material, solid, liquid or gaseous, is negated by the flashing of the arcs amid the relatively slowly rising and perfectly undisturbed volutes of vapor and detritus as well as by their direction of propagation, which is outward and downward as well as upward. On the other hand, any attempt at explanation on the basis of Hertzian or electromagnetic effects, due possibly to stress relief, etc. must also be excluded on the speed basis, which now becomes much too low.

After all is said, is there any real difficulty in accounting for the flashing arcs on the basis of the proposed hypothesis? Sound is propagated in air by compressional-rarefactional waves projected normally. The conditions for the production of the arcs are sudden explosions on a large scale. Given these in sufficiency, may we not imagine that in the resulting aerial condensational-rarefactional wave—or sheet of superposed waves—the refractive and reflective indices will be so altered as to form in bright daylight a zone visible by contrast, especially when viewed longitudinally, *i. e.*, through the edges of the transparent sphere? We are familiar with the visibility by contrast of the refrangibility of hot and cold air, and it would seem that mechanically engendered compressional-rarefactional aerial waves should be visible in the same manner if sufficiently accentuated. It is a question of the *degree* of condensation and rarefaction and this evidently depends directly on the power and inversely on the time factor. The proposition will be more truly scientific and possibly more acceptable if stated thus: An explosion propagates normal condensational-rarefactional waves in air—these are perceived by the ear as sound and may also be visible by unequal refraction when sufficiently powerful.

The writer publishes this brief reference to a phenomenon which he has twice been privileged to witness with the feeling—so common in cases of this nature—that he may be stating that

with which many are already familiar. He trusts that this is so and that the flashing arcs have been observed, whether by volcanologists or during experiments with high explosives. The only difficulty in the way of their being produced artificially would seem to be that of giving to them a sufficient size to ensure visibility. A charge of dynamite exploded in an open mortar would imitate the volcanic conditions, but on a small scale.

As observed by the writer at Vesuvius and Etna, the flashing arcs may be considered one of the most beautiful of all volcanic phenomena.

Naples, May 27, 1912.

ART. XXXIII.—*The Comparison of Two Screws*;* by CARL BARUS.

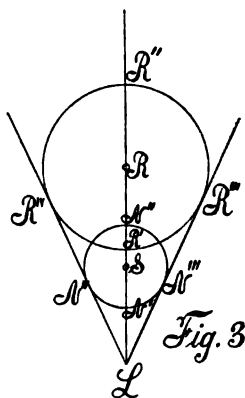
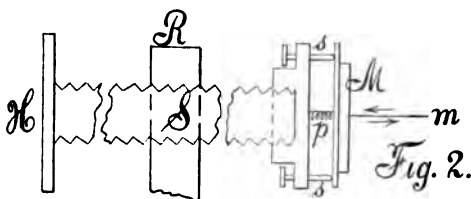
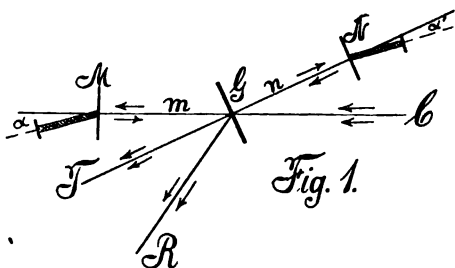
1. *Introductory*.—In work where two lengths are to be compared, a shift ΔN measured with one micrometer, for instance, and a thickness e with another (a caliper screw), it becomes of importance to coördinate these data directly. This may be done with facility by mounting the opaque mirrors M and N of an interferometer of the displacement type† on the two screws in question, shifting the ellipses away from the spectrum line with the first screw at N and returning them to the identical line with the other screw at M , through successive consecutive steps of their length. The screws must now be identically reversed in relation to the fixed beam of light and a similar series of complete data investigated. The true relation is the geometric mean of the two results, at each step.

2. *Method*.—In fig. 1 let M and N be the opaque mirrors, actuated by the micrometer screws at an angle α and α' respectively, to the beams of light m and n , i. e., the normals of the mirrors. C is the collimator, G the grating, and T the telescope. Let the latter be clamped, so that the direction TG is fixed throughout the experiment, as is also CG . It must be possible to remove the mirrors M and N , together with their micrometer screws, without changing the angles α and α' in

*Reprint abridged from a forthcoming Report to the Carnegie Institution of Washington, D. C.

† This Journal, xxxiii, pp. 109-119, 1912.

Fig. 1.



order that they may be identically reversed. Let S be the pitch of the screw at N , for instance, s the corresponding equivalent (often approximate pitch) at N' . Then

$$(1) \quad S \cos \alpha = s \cos \alpha'$$

Now let the mirrors be reversed, the angles α and α' and the beams m and n being reproduced, in virtue of the fixed direction GT . In this case

$$(2) \quad S \cos \alpha' = s \cos \alpha$$

Hence

$$(3) \quad S^2 = ss' = s^2 (1 + k).$$

Since k is very small

$$(4) \quad S = s_-(1 + k/2) = \frac{1}{2}(s + s'), \text{ nearly.}$$

In order that the reversal may be properly made, the tablets carrying the micrometers M and N with the attached mirrors should be truly horizontal, so that merely an adjustment of each in azimuth is necessary. The sharp white line which is the direct reflection from the mirror N is first restored to the cross hairs of the fixed telescope, after which the reflection from M is restored to the same image, the two lines merging into a single vertical sharp line. The slit images should now

also coincide horizontally in the field, *i. e.*, the two images of any specks of dust or cross lines in the slit should cover each other. If this is not the case the tablets carrying *M* and *N* must be provided with three adjustment screws, so that the condition of mirror normal to the beams of light may be reëstablished without changing *a* and *a'*. In other words, the adjustment screws of the mirrors on the micrometer must be left untouched.

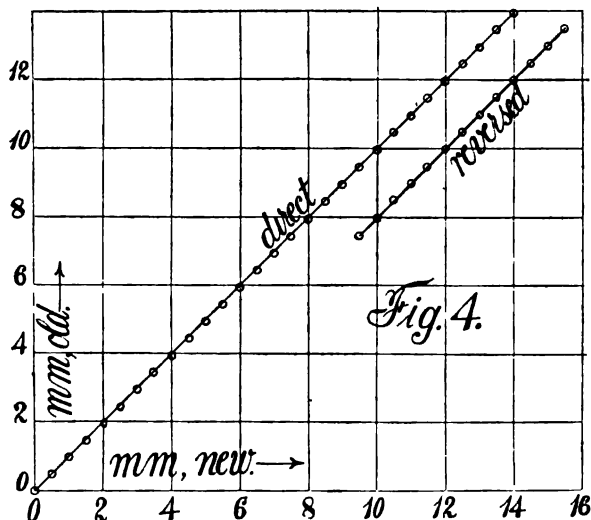
When this is done, the ellipses will be seen in the direction of the refracted rays *R* as soon as the proper distances *m* and *n* have also been reëstablished, by moving either mirror alone. The arrangement of mirrors on the tablet should therefore be as nearly as possible symmetric, even when different forms of screws are compared.

A simple type of micrometer screw or attachment suitable to any screw to be tested will also be used below and may be described here. *S*, fig. 2, is the micrometer screw in question, with its graduated head at *H* revolvable in the socket *R*, this being adjustable, with three screws as usual, on the tablet at either *N* or *M*, fig. 1. The mirror *M*, fig. 2, is separately adjustable with three screws (horizontal and vertical axes), *s*, *s*, and a strong spring suggested at *p*. The whole arrangement *Mps* is firmly fixed to the end of the screw *S*. In this case the mirror rotates with the screw as it advances and the latter is therefore necessarily normal to the component beam *m*, an adjustment secured by the set screws at *s* in the usual way, the effect of the operations being observed in the telescope *T* in fig. 1. The approximate adjustment is conveniently made with sunlight returned by reflection from the mirror to a screen 20 or 30 feet distant. Suppose, fig. 3, the mirror is nearly normal to the screw; let the intersection of the incident ray, the screw axis, the normals, and the reflected rays with the screen, all lines prolonged if necessary, be at *L*, *S*, *N'* and *R*, respectively. If the screw is rotated 360°, the normal will trace a circle *N'* to *N'^{IV}*, the reflected ray a similar circle *R'* to *R'^{IV}*. If the normal *N'* coincides with the axis of the screw *S*, the reflected ray will be at the center, *R*, of the circle *R'R''*. Hence the center is to be sought by rotating the screw. The mirror is now adjusted so that the reflected ray is at *R*. Then *N* is at *S*, as required. With successive trials this succeeds very well.

3. *Data*.—A trial comparison was made of the screws of two slide micrometers, one of them old but with an excellent slide, the other with a good new screw but an imperfect slide. As a result of this it was impossible to keep the ellipses adequately sharp throughout the whole motion of the screw. In fact, it was necessary to make a readjustment of mirrors *M* and *N* from

time to time, *i. e.*, to take a fresh start, so that the comparison proceeded rather in sections. Moreover, the motion of the slide not strictly parallel to itself appears in the data as an error of the screw and virtually it is so. The discrepancy may, however, be corrected without reestablishing a fresh zero, by removing the effect of any slight rotation at one mirror, due to an imperfect slide or other causes, by adjustment screws at the tablet of the other mirror, until the sharp lines of the ellipses are quite restored. In fact, this is a method of compensation, by which excess of length due to incidental rotation at one mirror is manually imparted to the other. Care must be taken to keep the angles α and α' unchanged. In other respects the comparison so far as the experiment is concerned was satisfactory (see fig. 4), very little difficulty in adjusting

FIG. 4.



and reversing being encountered. With two good slides the work would have proceeded smoothly from end to end of the screws, which were several inches long.

The first screw had a pitch of .05 centimeter, the micrometer reading to .00010 centimeter; the second a pitch of .025 centimeter, the micrometer reading to .00005 centimeter. The former was turned in steps of a single pitch, and the value which brought the center of ellipses, originally coincident with the given Fraunhofer line, back to coincide with it was read off on the finer screw.

For the reasons stated it was necessary to coördinate the successive sections of the measurements made and a fresh fiducial mark was determined in terms of the preceding whenever the ellipses lost adequate clearness. To find the relation of the two screws, the mean of the initial and final halves of each series was computed by deducting the corresponding observations from each other and averaging the result. In this way the ratio r of the old appears in

$$\begin{array}{ll} \text{Series I} & \dots\dots\dots r' = .9962 \\ \text{" II (mirrors reversed)} & \dots\dots r'' = .9997 \end{array}$$

Thus the true relation is finally

$$r = (r' + r'') / 2 = .9980$$

Usually a large part of the difference of values of the two screws is to be ascribed to the angles of alignment a and a' , if no special means are taken to orientate them accurately. With the ratio $r = S/s$ given, the ratio of the alignment angles would follow, but this is of little value. In fact, if

$$a' = a + da \qquad da = (1 - r) \frac{2 - a^2}{2a}$$

where a^2 may be neglected in comparison with 2. Hence da increases as a decreases, numerically. The real problem of finding a for the measuring micrometer is naturally not touched by such a method, in case of two slide micrometers. It is given at once, however, when one of the micrometers is of the form of fig. 2, where a' (say) is necessarily zero. Hence if the screws are identical $\cos a = 1/r$. Virtually, however, $S \cos a = s$ is the effective absolute value of the micrometer screw calibrated in this way in terms of s . This is a particular reason for the development of such an apparatus, fig. 2, to serve the purposes of comparison and standardization.

4. *Conclusion.*—The advantage of the present method is that steps of any size, quite arbitrarily, are admissible and there is no danger of ever losing count. A rigorously linear slide is presupposed. If the slide is slightly circular, even with very large radius, the ellipses are soon blurred and lost. To restore the ellipses by rotation of mirror is possible, but in any case precarious.

Brown University, Providence, R. I.

ART. XXXIV.—I. *On Some Growth Stages in Naticopsis altonensis*, McChesney*; by GEORGE H. GIRTY. With Plate I, figs. 1-8.

THE object of this paper is to call attention to certain striking changes in shape and sculpture shown in the development of one of our common Pennsylvanian species of *Naticopsis*, representing stages so distinct that they might be easily mistaken for different species, although to my knowledge no such mistake can be cited. It is possible, however, from the material at hand to connect all these aspects with a single specific type.

The species in question is familiar to everyone, though no one can be quite sure, as a matter of synonymy, just what name to call it by. As *Naticopsis altonensis* it is perhaps as familiar as by any other designation.

A chief feature of the mature form is its elongated shape and the strong deflection of the surface which takes place between the periphery and the suture and gives the final volution a strongly sinuous outline. The upper portion of this volution is marked by rather strong regular plications extending downward from the suture with a slight backward slope.

In following the mature form to its more youthful stages, I find that the lateral sinus first disappears and then the sub-sutural plications, so that we have in the beginning an unornamented shell with regularly formed whorls, then an ornamented shell with regularly formed whorls, and lastly an ornamented shell with sinuated whorls.

The first condition is maintained until about four volutions have been formed, and a height of 7^{mm} attained. The shape is rather elongated and the spire relatively high for the genus. The volutions are regularly rounded and marked only by fine incremental lines. Some specimens, however, show also extremely delicate revolving lines, so fine and obscure as to suggest their origin in a fibrous structure of the shell rather than in a system of sculpture.

The second condition occupies scarcely more than a single volution. The plications or fasciculated growth-lines below the suture are introduced gradually, but are rather rapidly developed. A specimen exemplifying this stage completed has a height of about 11^{mm}.

The final condition, in which is introduced the second feature of the mature shell, the lateral sinus, occupies two or more volutions, the enlargement being rapid (especially as to length), so that the dimension must have been 55^{mm} or

* Published by permission of the Director of the U. S. Geological Survey.

more, as indicated by a specimen in my collection. The variety *gigantea* in a figure by Meek and Worthen is over 60^{mm} long.

The specimens furnishing these data were collected near Garland, Henry County, Missouri.

II. Notice of a Mississippian gasteropod retaining coloration.*

Plate I, figs. 9–11.

The student of fossil shells has small chance to forget that the material which he is studying has suffered a loss of characters, and none of these is probably more early and more completely obliterated than that of coloration. Thus the paleontologist is deprived of this important aid in discriminating and identifying species. This is almost as true of the most recent fossils as of the most ancient, yet even in the Paleozoic an occasional specimen is found which retains traces more or less distinct of the original color ornamentation. Such specimens are, however, extremely rare,† and in the course of an experience which has brought under my observation certainly many hundred thousand examples, the specimen which is the subject of the present note is the only one of which it could be stated positively and unmistakably that the original markings were retained. Even in this instance, however, we can be sure only that the pattern and not the original colors are preserved. The ornamental pattern consists of more or less irregular zig-zag bands, the colors being alternately brown and whitish, and the definition surprisingly distinct. It is quite possible, of course, that the colors of the living shell may have been much less sombre.

The unique fossil showing this character was collected by Mr. Victor Barnett, near Tobinsport, Perry County, in southern Indiana, in rocks which have been referred to the Chester group. It is clearly a representative of the group of Paleozoic shells commonly referred to the genus *Naticopsis*, but in its specific relations it appears to be new. It consists of about three rapidly enlarging, regularly rounded whorls, which are deeply embracing so that the spire is quite low and almost the

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† The instances which I am able to mention of fossil shells in the Paleozoic retaining color markings are mostly brachiopods and mostly representatives of the *Terebratula* group. Davidson has figured several of these and recently D. K. Gregor (this Journal (4), vol. xxv, p. 313) has noticed an American species. The *Terebratulas* are colored in alternate enlarging rays. Kayser, as noted by Gregor, has recorded the retention of color markings on a Devonian *Rhynchonelloid*, and Waagen has figured two *Producti* as probably retaining their original color. These are *P. abichi* and *P. serialis*, which are represented as of a uniform dark reddish or brownish tint.

entire height is comprised in the body whorl. The sculpture consists of fine incremental lines which, near the suture, are somewhat stronger and fasciculated.

This form at once suggests *Naticopsis ziczac*, from about the same horizon in Ohio, but the suggestion is at once quenched by the fact that the zigzag markings in the present instance are clearly due to coloration and in the Ohio shell as clearly due to sculpture. In addition to this very important distinction, *Naticopsis ziczac* has a much higher spire. Aside from one or two forms which have been described but not figured, this species is most likely, from intrinsic characters as well as from its geologic position, to be identical with *Naticopsis littonana* var. *genevievensis*, itself known only from description unaccompanied by figures. Now the species *littonana* is not a *Naticopsis* and has never been referred to that genus save in this instance, so it seems probable that Meek really intended to write *carleyana*, which is a *Naticopsis* and was described at the same time as *Sphærodoma littonana* and from the same fauna. On this interpretation Meek's species may possibly prove to be the same as the one under consideration, though it is much larger. The two figures of *Naticopsis carleyana* given by Whitfield, though representing the same shell, are as differently shaped as if they were two distinct species. My specimen is quite similar to the one figure and quite unlike the other. Compared with specimens from Indiana which represent typical *N. carleyana*, my form has a lower spire and lacks the regular costæ or plications below the suture, though at the same time showing the growth lines more definitely. It is also much larger while composed of the same number of volutions. Because of the coloration, which can not, of course, be used as a specific character, it is proposed to call this form *Naticopsis picta*.

DESCRIPTION OF PLATE I.

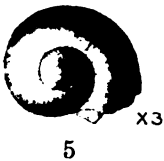
Naticopsis altonensis McChesney (p. 338).

FIGS. 1, 2, 3, 4. Side views of four specimens showing changes in shape and sculpture to maturity. Figures 1 and 2 are enlarged to three diameters.

FIGS. 5, 6, 7, 8. The same specimens, seen from above. Figures 5 and 6 are enlarged similarly to figs. 1 and 2. All four specimens are from the Pennsylvanian of Henry, Garland Co., Mo.

Naticopsis picta n. sp. (p. 340).

FIGS. 9, 10, 11. Three views of a specimen showing well-preserved color markings. Figure 9 is enlarged to two diameters. The specimen is from the Chester group near Tobinsport, Perry Co., Indiana.



ART. XXXV.—*The Sulphides of Zinc, Cadmium, and Mercury; their Crystalline Forms and Genetic Conditions*; by E. T. ALLEN and J. L. CRENSHAW. *Microscopic Study* by H. E. MERWIN.

INTRODUCTION.

MINERAL genesis in its fullest sense includes not only a knowledge of the limiting conditions outside of which a mineral can not exist, but a knowledge of the particular processes within the above limits by which the mineral is actually formed in the earth's crust. Concerning the first half of the problem,—the limiting conditions, the general relations of composition, temperature and pressure are pretty well understood, in so far as they have to do with equilibria. In equilibrium studies, however, *unstable forms* are commonly overlooked or avoided, but they must be taken account of in mineral genesis because many minerals are unstable forms. They differ from the unstable forms best known to chemists in their greater inertness; indeed, they often appear capable of unlimited existence at ordinary temperatures, though there is a potential difference between them and truly stable forms. For unstable forms an upper limit of temperature may be set, above which they can not exist. This is found experimentally by a determination of the lowest temperature at which, *under the most unfavorable conditions*, transformation into the stable form can be followed. We say "under the most unfavorable conditions," because the nature of the system in which the mineral undergoes transformation vitally affects the rate of the latter. Heating *alone*, i. e., without the addition of any solvent substance, is in general the condition most unfavorable to change. The velocity of the change would then be at a minimum and the temperature at which it first became noticeable would mark the upper limit of the actual existence of the mineral, above which it could never be formed.* This temperature is evidently not a sharp point, but it is, at least in some cases, a valuable limit in geology.

The effect of pressure on reversible changes is comparatively slight, in general, in systems containing no gaseous phase, though it may be considerable on minerals formed at great depths. In systems which contain a gaseous phase, the mass law affords us a guide to the influence of pressure. It may be noted here, by way of example, that in the formation of sulphides with hydrogen sulphide, a variation in the pressure of the latter only affects the quantity, not the nature of the solid phase, and while it would also condition the concentration

* Unstable forms may sometimes be obtained in the laboratory at temperatures where a slight disturbance is sufficient to effect their transformation, but it is hardly to be supposed that anything of this sort occurs in nature.

of the metal of the sulphide in the liquid phase, the absolute amount of the variation in most cases would be very small on account of the virtual insolubility of most mineral sulphides. Comparatively soluble sulphides like zinc sulphide are exceptional.

A comprehensive knowledge of necessary or even sufficient conditions of composition in mineral genesis is limited by the meagerness of what we know of chemical affinities. In practice, we must be content with the investigation of those systems which by reason of their simplicity or the light they are likely to throw on natural phenomena are especially promising. The method of procedure will depend materially on the class of minerals we have to study; e. g., if we have under consideration a *magmatic mineral*, the rock of which it is a constituent is a partial guide to the composition of the solution in which it crystallized, although it must not be forgotten that important volatile and soluble constituents may have escaped during the processes of rock formation. The best way to get light on the genesis of such a mineral is doubtless to study the behavior of systems made up of components, generally oxides, which we find in the rock. If, however, the mineral in question is a *vein mineral*, we have no similar indication of the composition of the original solution. Still, all lines of evidence indicate that the solution must have been aqueous and that the constituent elements of the mineral existed usually in more complex forms than those in the magmatic solutions. Thus the sulphur of a sulphide may have existed originally as hydrogen sulphide, soluble sulphides, sulphates or even more complex forms, while the metal doubtless occurred in the form of some salt. Now, while we might obtain valuable chemical information by the investigation of systems consisting of sulphur and the various metals, it would not be very helpful in the elucidation of geological processes. To get at the composition of the systems in which vein minerals have formed, we must rely rather on our knowledge of the composition of springs and mine waters and on our knowledge of general chemistry. At the same time, important subsidiary information may be obtained by the study of various other systems adapted especially to the case in hand.

The determination of the geological portion of the subject of mineral genesis might be left entirely to the geologist; but it will be evident to anyone that there are decided advantages in the study of these questions by a method of consultation between the laboratory and the field worker—a method which affords opportunities for mutual suggestion and criticism, and promises safer conclusions.

The necessary and sufficient conditions for the formation of the sulphides of zinc, cadmium, and mercury which are stated in these pages have been worked out with geological aid from

several members of the U. S. Geological Survey, who will be specially mentioned as occasion demands.

I. THE SULPHIDES OF ZINC: SPHALERITE AND WURTZITE.

The sulphide of zinc occurs in nature crystallized in two different forms, the common sphalerite, or blende, which belongs to the regular system and the comparatively rare wurtzite which belongs to the hexagonal system. Both are transparent and straw-colored* when pure and are distinguished from each other and from amorphous zinc sulphide by the presence or absence of double refraction† and by the magnitude of the indices of refraction. The latter for sphalerite is 2.37, which in sodium light is slightly less than that of wurtzite for the ray vibrating in the vertical axis, while the other index of the latter mineral is 2.35 (Merwin). These properties were determined on a very pure natural sphalerite from Sonora, Mexico, and on the wurtzite formed from it by heating to the proper temperature. The analysis of this mineral was as follows:

Zn	66.98
Fe	0.15
S	32.78

99.91

The specific gravity of the two minerals was also determined on the same material by the pycnometer method at 25°.

TABLE I.
Specific gravities of Sphalerite and Wurtzite.

Sphalerite. ¹			Wurtzite.	
I. Sonora, Mex.	II. Same locality.		Formed by heating sphalerite	
mineral at 25° water at 25°	mineral at 25° water at 25°	mineral at 25° water at 4°	mineral at 25° water at 25°	mineral at 25° water at 4°
4.101	4.103	----	4.098	----
4.102	4.102	----	4.100	----
4.100	4.102	----	4.098	----
4.099	----	----	4.098	----
4.001	----	----	4.100	----
av. 4.100	av. 4.102	av. 4.090	av. 4.099	av. 4.087

¹ For the determination of sample I, only about 6.5 g. were used; for those of sample II, about 18 g. was available, and the latter values are subject to less error in consequence.

* The blende from Franklin, N. J., and from Nordmark, Sweden, is described as pure white. (Dana, A Textbook of Mineralogy, 1906, p. 61.) Our purest synthetic products have all been straw-color.

† For an interesting exception to isotropy in amorphous bodies see microscopic part of this paper, p. 383.

It appears from the above data that the specific gravities of sphalerite and wurtzite of identical composition are nearly the same, but that of wurtzite is very slightly lower.

Enantiotropic relation between Sphalerite and Wurtzite.

If sphalerite is heated to a temperature of about 1100° and cooled with moderate rapidity, i. e., to 100° inside of two hours, microscopic examination shows that it is completely transformed into wurtzite.* The heating curve, however, shows no break to indicate that any heat change has accompanied the transformation. A very careful test of this point was made as follows:†

FIG. 1.

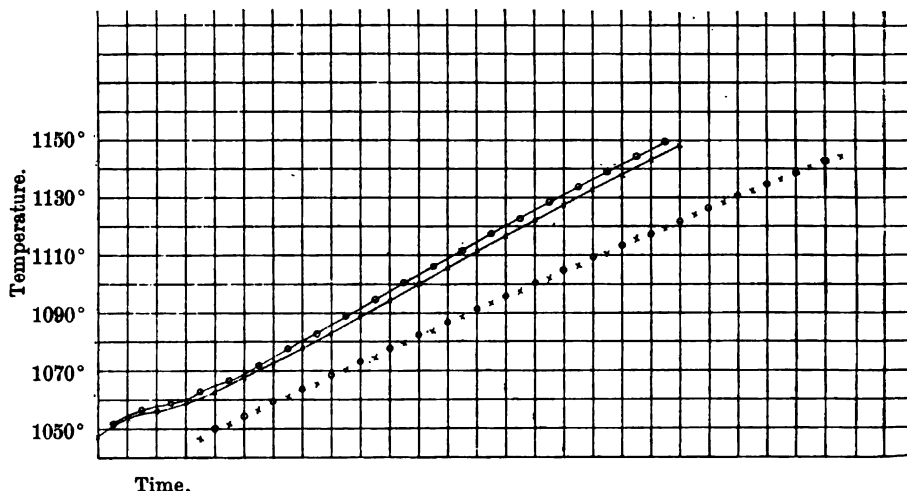


FIG. 1. Heating curves for sphalerite and wurtzite in the vicinity of the inversion point. $\times \times$ Sphalerite, $\circ \circ$ Wurtzite.

Two small cylindrical crucibles, one containing 10 g. sphalerite and the other 10 g. wurtzite, each provided with a calibrated thermoelement, were heated side by side in the same furnace, the temperature of the two elements being read alternately every half-minute. By reference to the curves in fig. 1, it is seen that those of the first pair are practically parallel; those of the second pair are virtually identical, i. e., the temperature of the two crucibles, by reason of their position in the furnace, was a little closer together in the second case. Neither pair

* J. Weber heated small plates of sphalerite in a Bunsen flame and cooled quickly. He found they had become anisotropic. *Zs. Kryst.*, xlv, 212, 1908. Biltz expressed the opinion that sphalerite might change to wurtzite without sublimation. *Zs. anorg. Ch.*, lix, 273, 1908.

† See W. P. White, this Journal, xxviii, 488, 1909.

shows any lagging of one curve behind the other to indicate any absorption or evolution of heat in either substance.

The temperature interval which is included by the curves will be found by comparison with the sequel to lie *above* the true inversion point. It was found, however, by actual trials that the transformation was subject to hysteresis and, on comparatively rapid heating, occurred in this interval. The reaction sphalerite \rightleftharpoons wurtzite was proved to be reversible by long heating at selected temperatures (see below), and consequently there must be a heat absorption when sphalerite is heated; and further, since the change was found to be complete inside of a time interval of six minutes and a temperature interval of 70° , this effect must be quite small. The inversion point was determined with considerable accuracy by long heats at measured temperatures, after which the direction of the change was determined microscopically. The sluggish nature of the change from wurtzite to sphalerite made it possible to cool the former to room temperature without any transformation into sphalerite. By continually narrowing down the temperature interval on either side of which the transformation was reversed, the inversion point was determined within $\pm 5^\circ$.

The apparatus* used for most of the work consisted of a tube of Berlin porcelain 25^{mm} inside diameter and 500^{mm} long, closed at one end and glazed inside and out. The tube, which was held in a vertical position, was closed at the top by a doubly perforated graphite cover. Through the central orifice passed a glazed Marquardt tube of 6^{mm} internal diameter, also closed at one end, which protected the thermoelement. Attached to the closed end were one or more short tubes, also closed at one end, of the same size and material, which contained the zinc sulphide in the form of coarse powder. The large enclosing tube was traversed by a current of dry hydrogen sulphide, which entered by a second Marquardt tube open at both ends. The heating was done by a resistance furnace which surrounded the cylinder.

The thermocouple which was used for the final temperature measurements was calibrated after they were finished, at the silver point (960°).

By reference to Table II it will be seen that the inversion point of zinc sulphide may be located between 1015° and 1024° , i. e., $1020^\circ \pm 5^\circ$. As was mentioned above, the reversion of wurtzite to sphalerite is very slow. Instead of heating in an atmosphere of hydrogen sulphide, it was naturally more convenient in long continuous heats to use a vacuum apparatus.†

* Allen, Crenshaw and Johnston, this Journal, xxxiii, 195, 1912.

† Ibid., xxxiii, 210, 1912.

TABLE II.
Inversion of pure natural zinc sulphide.

	Time.	Temp. in mv.	Temp. in degrees	Result.
1	4 hrs.	9950 El. A.	1037	{ Wurtzite unchanged. Sphalerite about $\frac{1}{3}$ changed.
2	3 $\frac{1}{4}$ "	9650 El. A.	1011	" unchanged.
3	4 "	9850 El. A.	1028	" slightly changed.
4	4 $\frac{1}{2}$ "	9800 El. A.	1024	" very slightly changed.
5	3 $\frac{3}{4}$ "	9750 El. A.	1020	{ Wurtzite slightly, if at all, changed. Sphalerite unchanged.
6	9 $\frac{1}{8}$ "	9700 El. A.	1015	{ Sphalerite unchanged. Wurtzite partly changed.

In four hours at 800° there was no appreciable change in wurtzite. It required 66 hours, between 800° and 900°, to change the mineral entirely into sphalerite. In a repetition of the experiments, 48 hours were required for the change at 850°–900°, and again 40 hours at 850°–950°. For these experiments we used both the wurtzite formed by heating pure natural sphalerite and also some natural wurtzite crystals from the Hornsilver Mine near Frisco, Beaver Co., Utah, which behaved in the same way.

Effect of iron on the inversion point of zinc sulphide.

It is well known that the natural sulphide of zinc nearly always contains sulphide of iron (FeS), sometimes in quantities as high as 20 per cent or more. The effect of this common impurity on the inversion point was thought to be of interest, and accordingly several iron-bearing sphalerites which contained only small quantities of other impurities were carefully analyzed and tested thermally.

Ferrous sulphide lowers the inversion point of sphalerite strongly as the results in Table III show. From fig. 2 it will be seen that the inversion temperatures when plotted against the percentages of iron form a fairly regular curve. It ought to be noted, however, that blende containing other impurities besides iron sulphide does not always show a lower inversion temperature than pure sphalerite. Thus a blende from

TABLE III.

Influence of iron on the inversion temperature of sphalerite.

	I	II	III	IV	V
Locality	Sonora, Mex.	Scotland	Guipuzcoa, Spain	Queensland, Australia	Breitenbrunn, Saxony
Impurities {	Quartz.....	0.33%	----	----	----
	Pyrite.....	----	----	----	3.0 %
	Copper.....	0.13	0.22	----	0.10
	Manganese.....	----	tr	0.20	1.05
Percentage of iron.....	0.15	1.43	5.47	10.8	17.06
Inversion temperature....	1020°	998°	955°	919°	880°

Oporto, Portugal, containing 7.43 per cent iron, 0.68 per cent cadmium and traces of lead and silver, was tested repeatedly and found to have an inversion temperature of 1035° as compared to 1020° for pure sphalerite.

The specific gravities of these blendes were also determined and from them the specific volumes were calculated.

TABLE IV.

Influence of ferrous sulphide on the specific gravity of sphalerite.

	I	II	III	IV	V
Locality	Sonora, Mex.	Scotland	Guipuzcoa, Spain	Queensland, Australia	Breitenbrunn, Saxony
Percentage of iron..	0.15%	1.43%	5.47%	10.8%	17.06
Sp. gr. at 25°.....	4.102	2.091	4.035	3.99†	3.970
Sp. gr. corrected....	----	----	4.042*	----	3.946‡
Density mineral at 25°	4.090	4.079	4.030	3.98	3.935
water at 4°.....	0.2444	0.2451	0.2481	0.2513	0.2541

* Corrected for 0.33 per cent quartz, sp. gr. 2.65 (see Table III).

† Only 3.5 grms. were available for this determination; hence the gravity is given only to the second decimal.

‡ Corrected for 3 per cent pyrite, sp. gr. 5.02 (see Table III), from which it was separated by dissolving in hydrochloric acid in a carbon dioxide atmosphere.

The impurities in these blends are all small except in V, and we are certainly justified in correcting the gravities for quartz and pyrite in III and V, respectively, since these impurities are mechanically mixed. The specific volumes plotted in fig. 3 show a nearly rectilinear relation. The dotted line on the plot is drawn through the specific volumes of ZnS and

FIG. 2.

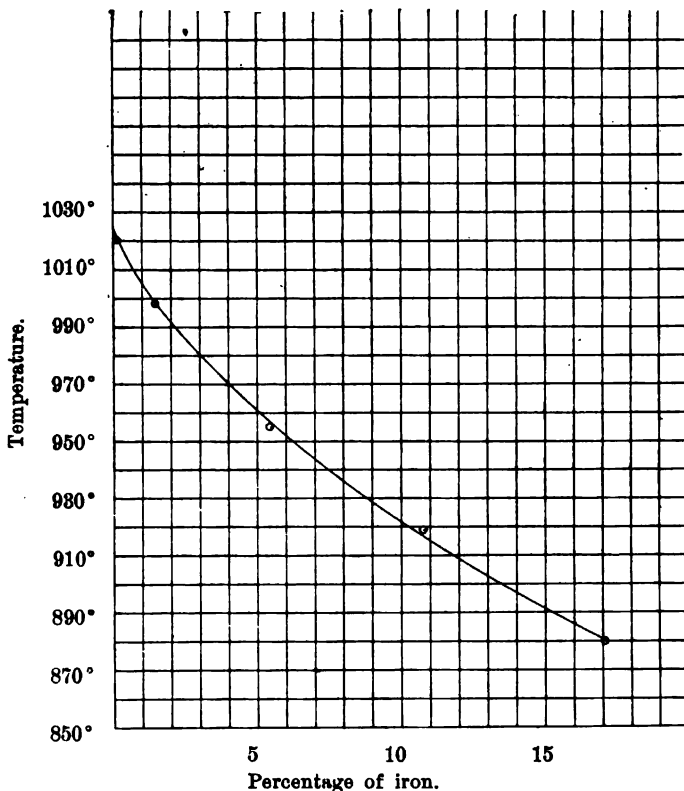


FIG. 2. Influence of iron on the inversion temperature of sphalerite.

FeS.* If we compare this with the locus of the actual specific volumes of the natural blends, it is evident that the solution of ferrous sulphide by sphalerite (ZnS) must be attended by a marked expansion.

For the relation of the indices of refraction of these solutions to their composition see microscopic part.

* See Allen, Crenshaw and Johnston, this Journal, xxxiii, 198, 1912.

The effect of solvents on the inversion point of ZnS.

When wurtzite is heated in a medium of molten chloride of sodium it changes to sphalerite much more rapidly than when heated in vacuo or in an atmosphere of hydrogen sulphide. Not only did the wurtzite change in the solid state, but new dodecahedrons of the refractivity 2.37 were formed. As the

FIG. 3.

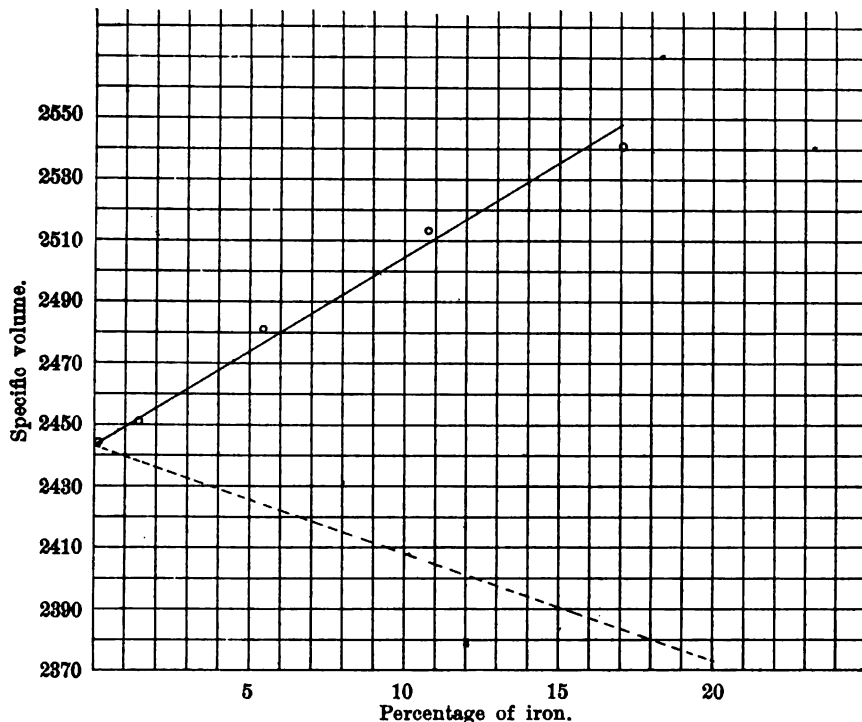


FIG. 3. Influence of iron on the specific volume of sphalerite.

surface of the salt was left open to the air a little zinc oxide of lower refractive index than wurtzite was detected by the microscope. The aqueous solution of the sodium chloride gave strong tests for zinc and sulphate. This indicates the reaction $2\text{NaCl} + \text{ZnS} = \text{ZnCl}_2 + \text{Na}_2\text{S}$. The reversion of the reaction in the colder parts of the charge may have caused the deposition of the crystals which are the stable form at that temperature. In a platinum tube protected from the air by a slow stream of carbon dioxide, wurtzite was almost completely changed to sphalerite in 30 hours and excellent small dodecahedrons were obtained. Pure amorphous zinc sulphide in 46

hours crystallized from the same solvent in still larger crystals. The temperature in nearly all these experiments was very near the melting point of sodium chloride, slightly above 800° . Schneider* formed crystalline zinc sulphide by heating 1 part of pure dry amorphous zinc sulphide with 12 parts potassium carbonate and 12 parts sulphur. A repetition of this experiment confirmed Schneider's statement. Larger crystals than those from sodium chloride were obtained in this way at about 400° . Both dodecahedrons and tetrahedrons were observed.

Thermal behavior of ZnS above its inversion point.

Cussak † states that zinc sulphide melts at 1064° . No other investigator has ever observed the melting of zinc sulphide, though several have obtained wurtzite as a sublimation product. ‡ The results of Hautefeuille are especially interesting since he obtained well-characterized hemimorphic crystals like those of nature by subliming zinc sulphide in a bed of alumina. We found zinc sulphide volatile enough at about 1000° to form small crystals of wurtzite in a few hours. Several grams were sublimed in well-formed crystals of considerable size between 1200° and 1800° . We observed no melting under any circumstances at atmospheric pressure. The experiment was tried of dipping a tube containing zinc sulphide quickly into a furnace heated to 1550° . It was thought that if this temperature were above the melting point, deorientation might go on faster than volatilization, but no certain indication of melting was found.

Zinc sulphide from aqueous solutions.

It has been shown in the foregoing pages that zinc sulphide may exist in two enantiotropic forms; β -ZnS, or sphalerite, stable below 1020° , and α -ZnS, or wurtzite, stable above 1020° . Nevertheless the latter as well as the former may be crystallized at comparatively low temperatures from aqueous solutions, and the necessary conditions for the formation of each are of the highest interest to chemical geology. Zinc sulphide is surprisingly difficult to crystallize below 200° and it is safe to say neither sphalerite nor wurtzite has been obtained heretofore in the wet way.

Sphalerite from aqueous solutions.

Several investigators claimed to have obtained sphalerite from water solutions. Baubigny§ is said to have formed

* Jour. prakt. Chem. (2), viii, 33, 1874.

† N. J. Min. 1899, I, Referate 196.

‡ Deville and Troost, C. R., lii, 920, 1861. Sidot, *ibid.*, lxii, 999, 1866; lxiii, 188, 1866. Hautefeuille, *ibid.*, xciii, 824, 1881. Mourlot, *ibid.*, cxxiii, 54, 1896. Biltz, *loc. cit.*

§ Fouquée et Levy, *Synthèse des Min. et Roches*, Paris, 1882, 298.

blende by heating to 80° , in a sealed tube, an acid solution of zinc sulphate, saturated with hydrogen sulphide. We prepared many products in a similar way and none of them ever showed an index of refraction greater than about 2.25, which is characteristic of amorphous zinc sulphide.

Villiers * states that the precipitate from *alkaline* zinc solutions by hydrogen sulphide, though amorphous ordinarily, is crystallized by certain influences, e.g. by the presence of a large excess of ammonium chloride in the solution from which it is precipitated. Heat also transforms the gelatinous precipitate into a distinctly granular state, in which, though it does not show any appearance of crystallinity, it is probably cubic because it possesses a decidedly lower solubility than the gelatinous mass at first formed. Precipitates which we obtained in this way were also amorphous.

Stanek † believed he had obtained a crystalline product when he heated amorphous zinc sulphide with colorless ammonium sulphide to 150° – 200° , in sealed tubes.

Senarmont ‡ states that by heating the amorphous sulphide in sealed tubes with hydrogen sulphide under a pressure of several atmospheres he obtained blende. The last-named investigators (Stanek and Senarmont) give no proof of their claims except the appearance of the product. Their experiments, repeated by us more than once, gave nothing but amorphous sulphide. No crystal outlines appeared under the microscope, and when the grains were coarse enough to admit of the measurement they showed a refractivity of 2.2 to 2.3 instead of 2.37. Having failed to accomplish our purpose by any methods given in the literature, we experimented with alkali sulphides in sealed tubes with the result that only amorphous products were obtained at first and when the tubes were heated for long periods or at higher temperatures (250° and above) they were so badly attacked, that the method was temporarily abandoned. Meanwhile other methods were tried.

Action of sodium thiosulphate on Zinc salts.

Our success with the use of thiosulphate in the preparation of the mercuric sulphides gave us some hope that it might prove satisfactory here. Sodium thiosulphate in excess shows no action on zinc salts in the cold, but on heating to 100° the zinc is quantitatively precipitated in dense form, which under the microscope appears in spherical aggregations. This is amorphous, however. Though in one instance there seemed to be slight double refraction as if from wurtzite, the refractive index was too low. The principal reaction here, gives rise only

* C. R., cxx, 189, 498, 1895.

† Zs. anorg. Ch., xvii, 117, 1898.

‡ Ann. Ch. Ph., xxxii, 129, 1851.

to neutral products, though by a secondary reaction we have usually a very little sulphur dioxide formed. The reaction is the same as with ferrous * salts with excess of thiosulphate, and was worked out in the same way, i.e. weighed quantities of the substances were introduced in solution into glass tubes which were exhausted of air, sealed and heated to a certain temperature. On cooling, the precipitate was filtered and washed with water, then with alcohol and dried in the air. The sulphur in it was removed by carbon disulphide. The filtrate was diluted to a definite volume and aliquot parts tested for zinc, free acid and finally unchanged thiosulphate by a standard iodine solution. The following table (Table V) shows the results obtained compared with those calculated for the reaction $4\text{Na}_2\text{S}_2\text{O}_3 + \text{ZnSO}_4 = 4\text{Na}_2\text{SO}_4 + \text{ZnS} + 4\text{S}$.

TABLE V.
Action of $\text{Na}_2\text{S}_2\text{O}_3$ on zinc salts.

No.	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ taken	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ taken	Water	Tem- pera- ture	$\text{ZnS} + \text{S}$		ZnS		$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ consumed	
					Found	Cal.	Found	Cal.	Found	Cal.
1	2.000g	8.000g	75 cc	100°	1.59	1.57	.67	.68	6.99	6.95
2	2.000g	8.000g	"	"	1.56	"	.67	"	6.76	"
3	2.000g	8.000g	"	"	1.51	"	.68	"	6.35	"
4	2.000g	8.000g	"	"	1.59	"	.70	"	7.04	---

Some secondary reaction evidently affects the quantity of thiosulphate consumed, but a fuller investigation was not deemed advisable. Small quantities of sulphurous acid are formed, but not enough to cause the variations in 2 and 3. In No. 4, which was heated longer than usual (several days), a little hydrogen sulphide was formed, doubtless according to the equation $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_3 + \text{H}_2\text{S}$, which we have elsewhere established. The excess of thiosulphate would thus be reduced.

Attempt to form Sphalerite in other ways.

A number of other methods for the synthesis of sphalerite were tried in which zinc sulphide would be precipitated or crystallized in neutral or alkaline solution. Thus hydrogen sulphide was brought into contact with zinc carbonate and zinc bicarbonate; and amorphous zinc sulphide was heated with a solution of sodium bicarbonate. In every case, no matter how slow the reaction, only amorphous sulphide was obtained. It will,

* Allen, Crenshaw and Johnston, this Journal, xxxiii, 185, 1912.

therefore, not be necessary to describe the experiments in detail. Two other experiments of a negative nature may also be mentioned here. The behavior of metallic zinc in saturated sulphurous acid solution gave only amorphous sulphide in rather large grains—of refractivity 2.2–2.3. On account of the weak nature of this acid it was thought sphalerite might possibly be formed. The action of powdered marcasite on zinc chloride in an atmosphere of carbon dioxide gave no sulphide of zinc.

Formation of Sphalerite by precipitation with alkali sulphides.

The precipitate from zinc salts by alkali sulphides in the cold, or under ordinary conditions at a boiling temperature, shows no indications of crystallinity. However, when pretty concentrated solutions of the soluble sulphides act on amorphous zinc sulphide at higher temperatures, sphalerite is obtained. As previously stated, experiments with concentrated alkaline solutions gave much trouble. The glass tubes were so badly attacked that the products obtained in them were quite impure, greatly increasing the difficulties of microscopic analysis, while at 300° the tubes were sometimes eaten entirely through. The difficulty was finally overcome by putting the solutions into platinum tubes which were then set inside of glass tubes, the latter being afterwards sealed. Satisfactory platinum tubes which are not so expensive as to be prohibitive may be fashioned from foil by the use of the oxyhydrogen blowpipe. Ours had a diameter of about 15^{mm} and a total capacity of about 40^{cc}.

In our first successful experiment amorphous zinc sulphide was put into a tube of Jena combustion glass* with sodium sulphide of about 20 per cent concentration; the tube and its contents were heated 3 days in a steel bomb at 350°. Small though good crystals of sphalerite, both octahedrons and tetrahedrons, were obtained. Again, amorphous zinc sulphide was heated in a platinum tube sealed inside a glass tube, as described above, with potassium sulphide of about 35 per cent at 200° for 11 days. Minute tetrahedrons of sphalerite were obtained. A solution of 10 per cent potassium sulphide heated with amorphous zinc sulphide in a similar manner at 200° for two months† gave a product which was entirely crystallized in minute isotropic crystals with evident faces but rather rounded edges. A second experiment with 10 per cent sodium sulphide lasting six weeks at 100° failed to yield any crystals. Thus we find, as we should expect, that the lower the temperature and the more dilute the reagent the longer is the time required to

* Out of a large number of experiments with glass tubes, this was the only one in which the product could be recovered.

† By mistake the temperature was dropped to 100° for a part of the period.

produce recognizable crystals. *It is a notable fact that sphalerite only was obtained by this method, never wurtzite.*

Zinc sulphide from acid solutions.

When zinc sulphide is precipitated by hydrogen sulphide from solutions which are either neutral or acid at the start, at temperatures ranging from the ordinary up to 200°, the product is always amorphous so far as our observation goes. The double tube method, which proved so satisfactory in the formation of some other sulphides, did not generate hydrogen sulphide at a rate slow enough to give crystals. True, the products were frequently, though not always, doubly refracting, and for some time we were misled into the belief that they were wurtzite, but the measurement of their refractive index later on showed that they were in all probability amorphous and that the double refraction was caused by strains produced in the hardening of precipitates originally gelatinous. (See microscopic part.) Experience in qualitative analysis might lead one to believe that zinc salts could not be precipitated by hydrogen sulphide from solutions containing much free acid. As a matter of fact precipitates are obtained from rather strong acid solutions, provided only sufficient time is allowed, as Glixelli* has proved.

Table VI shows our own results on this point. In it are given the times which elapsed after hydrogen sulphide was introduced, before a precipitate was observed, and the composition of solutions after ten days' standing. The concentration of the zinc was 0.2 N at the beginning in all the solutions except the last; the hydrogen sulphide was kept at a pressure of approximately one atmosphere, by uncorking the flasks and passing in fresh gas from time to time, while the concentration of the sulphuric acid varied as stated in the table. The experiments were carried out at room temperature. It will be noted that a partial precipitation was obtained in the above manner from solutions which contained about 5 per cent sulphuric acid at the start, and nearly 6 per cent at the end of the experiment. With a higher initial concentration of zinc or a higher pressure of hydrogen sulphide, precipitation would naturally be obtained from solutions containing still more acid. The text-books commonly assume equilibrium in these systems and use them as examples of the mass law. Preliminary work on the subject has convinced us that such is not the case. In fig. 4 are plotted the concentrations of zinc in solution as they vary with the concentration of sulphuric acid, after the precipitation with one atmosphere of hydrogen sulphide has apparently ceased. If one begins with the same precipitate, adding different concentrations of acid and maintaining the hydrogen sulphide at one atmosphere, different results are obtained.

* Zs. anorg. Ch., 1v, 297, 1907.

More work on this subject is under consideration, but the results given show well enough that hydrogen sulphide will *in time* precipitate zinc from solutions which are quite strongly acid.

FIG. 4.

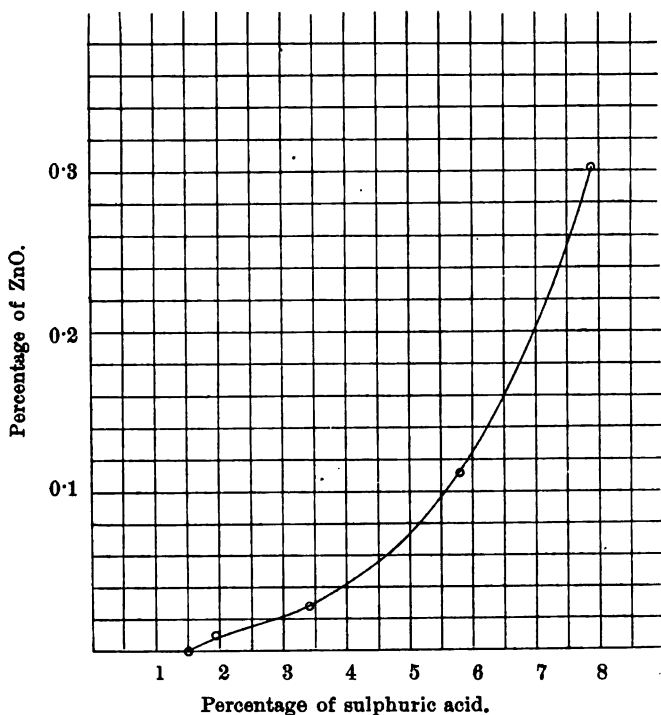


FIG. 4. Influence of free acid on the precipitation of zinc sulphide.

Crystalline zinc sulphide from acid solutions.

A great number of experiments have been made with the purpose of preparing crystalline zinc sulphide from acid solutions at *low* temperatures, yet so far without success. This seems very remarkable when we consider how slowly the sulphide forms in strong acid solutions (see Table VI), and we have as yet no explanation for it. At temperatures of 250° and upward, by the use of the double-tube method* crystalline products can be obtained. The results are sufficiently interesting to be stated in detail. In all the experiments the source of hydrogen sulphide was about 6 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 15–20^{cc} water, which was placed in the outside tube. The inside

* Allen, Crenshaw and Johnston, this Journal, xxxiii, 174, 1912.

TABLE VI.

The action of hydrogen sulphide on 0.2N ZnSO_4 , with varying concentration of H_2SO_4 .

No.	H_2SO_4		Approx. time before ppt. began	Zn in solution after 10 days		H_2SO_4 after ppt.	
	Normality	Per cent		Normality	Per cent	Normality	Per cent
1	0.1	0.49	1 min.	0.0000	0.000	0.300	1.47
2	0.2	0.98	5 min.	0.0031	0.010	0.398	1.95
3	0.5	2.45	25 min.	0.0089	0.029	0.691	3.39
4	1.0	4.90	a few hours	0.0338	0.111	1.183	5.80
5	1.5	7.36	no ppt. after 2 days	-----	-----	-----	-----
6*	1.5	7.36	3 days	0.0923	0.302	1.609	7.89

* Concentration of ZnSO_4 in No. 6 was increased to 0.214N after 2 days.

tube* in each case contained 10–15^{cc} of 10 per cent $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. The time in all cases was 2 to 3 days. The concentration of the sulphuric acid in the latter solutions and the temperature to which the tubes were heated varied in the different experiments.

Exp. 1. Temperature 300°–10% H_2SO_4 used. The product consisted of spherulitic aggregates, all doubly refracting and having the refractive index of wurtzite.

Exp. 2. Temperature 300°–7.5% H_2SO_4 . Crusts and spherules consisting of felted fibers which were unquestionably wurtzite sometimes surrounded by amorphous sulphide, indicating that the precipitate first formed was amorphous. 5–10 per cent of more transparent irregular masses of isotropic substance having the refractive index of sphalerite.

Exp. 3. Temperature 300°–5% H_2SO_4 . The product consisted of globules with crystal faces growing out of them. Nearly all were isotropic and showed the refractive index of sphalerite, though there was perhaps 5 per cent of doubly refracting wurtzite.

Exp. 4. Temperature 300°–4% H_2SO_4 . About 30 per cent amorphous sulphide, the rest wurtzite.

Exp. 5. Temperature 300°–1% H_2SO_4 . The product showed crystalline faces and was apparently isotropic. Practically all of it had the index of sphalerite, though there were a few pieces of amorphous material.

Exp. 6. Temperature 250°–5% H_2SO_4 . The product consisted almost entirely of large spherules showing both radial

* A platinum tube was used.

fibers and felted fibrous structure. Inside of some were nuclei of amorphous material, indicating again that the precipitate was at first amorphous. Crystalline material all wurtzite.

Exp. 7. Temperature 250° — 2.5% H_2SO_4 . Both large and small spherules, the last in clustered form and amorphous, the large ones mostly doubly refracting and crystalline wurtzite.

Exp. 8. Temperature 350° — 5% H_2SO_4 . Possibly 30 per cent wurtzite, the rest sphalerite.

Exp. 9. Temperature 350° — 10% H_2SO_4 . Perhaps 80 per cent wurtzite, the rest sphalerite.

Exp. 10. Temperature 350° — 2.5% H_2SO_4 . Most of the product consisted of small spherules, of which about 30 per cent was amorphous, the rest felted aggregates of wurtzite.

Exp. 11. Temperature 250° — 1% H_2SO_4 . Consisted almost wholly of irregular granules, much of it isotropic and having the refractive index of sphalerite. In strong light considerable of it shows double refraction and the index of wurtzite.

Exp. 12. Temperature 300° — 2.5% H_2SO_4 . All apparently isotropic irregular forms having the index of sphalerite.

TABLE VII.

Influence of temperature and acid concentration on the crystalline form of Zinc sulphide.

Temperature	Percentage of H_2SO_4					
	1.0	2.5	4.0	5.0	7.5	10.0
350°	----	70% wurtzite.	----	30% wurtzite.	----	80% wurtzite.
300°	no wurtzite; very little amorphous sulphide.	no wurtzite.	70% wurtzite; rest amorphous sulphide; no sphalerite.	5% wurtzite.	90% wurtzite	100% wurtzite.
250°	much sphalerite as well as wurtzite.	all wurtzite and amorphous sulphide.	----	all wurtzite and amorphous sulphide.	----	----

The results of these experiments are summarized in Table VII. When all the data are carefully compared, it will be seen that temperature and acid concentration appear to be the two fac-

tors which determine the product ; and if we omit two experiments out of the twelve done at three different temperatures, we find the following regularity : For a given temperature the higher the acid concentration the greater is the quantity of *wurtzite* found in the product, and for a given acid concentration the higher the temperature the greater is the quantity of *sphalerite* found in the product. More work ought to be done on this point, but the above conclusion gains support from the fact that the same rule proved true in the case of the disulphides of iron.* There the quantity of *pyrite* increased with the temperature for a given acid concentration, and the quantity of *marcasite* increased with the acid concentration for any given temperature. When it is remembered that pyrite and sphalerite are *stable* forms, while marcasite and wurtzite are *unstable*, the analogy becomes striking.

In one respect this synthetic work on sphalerite and wurtzite may appear inadequate to the geologist, viz., the temperature of formation. Field observation points to lower temperatures in many instances than the lowest at which we have succeeded in forming these minerals. Although it would be highly desirable to obtain positive results at lower temperatures, it may be pointed out that there is nothing in our knowledge of the minerals to indicate anything more than *continuous* changes in the necessary conditions as the temperature falls. We must admit, however, that the temperature interval is still too long to extrapolate accurately, so that we might predict, for example, what concentration of acid would be necessary at ordinary temperature to give rise to pure wurtzite. Since even quite dilute solutions of soluble sulphides and zinc salts always give an immediate amorphous precipitate at the ordinary temperature, and since amorphous sulphides are seldom met with in nature, we are constrained to believe that the natural sulphides which have been deposited even as low down as 100°, must have been crystallized from very dilute solutions indeed and therefore exceedingly slowly.

The genesis of the natural sulphides of zinc.

The sphalerite of deep veins has in all probability been formed from hot solutions, and the latter are generally alkaline, as we know both from field observation of hot springs and from our knowledge of the hydrolysis of alkali silicates, like the feldspars, with hot water. In accord with this we have found that alkaline solutions always give rise to sphalerite, never to wurtzite.

The conditions under which the sphalerite of the Mississippi Valley region was deposited have been much discussed by

* Allen, Crenshaw and Johnston, loc. cit., p. 179.

geologists. We may call attention, in this connection, to the fact that sphalerite can be formed from acid as well as alkaline solutions. If the temperature is as high as 300° , only sphalerite seems to be deposited from solutions containing 1 per cent of free sulphuric acid, while only a few per cent of wurtzite is formed when the concentration of acid is as high as 5 per cent. However, when the temperature drops to 250° a solution containing as much as 2.5 per cent acid deposits practically pure wurtzite. In other words, from 350° down to 250° , which is as low as we have been able to get crystalline products, the lower the temperature the smaller is the percentage of acid required to give pure wurtzite. Unfortunately we cannot say what that percentage may be at ordinary temperature, because we cannot imitate the slow rate of crystallization which presumably proceeds in nature. But certainly sphalerite may be what geologists call a secondary mineral if the temperature and acid concentration fall within certain limits. On the other hand, to judge from the synthetic work wurtzite can never be anything but a secondary mineral,* since we have obtained it only from acid solutions. Our knowledge of natural wurtzite is still rather limited. Mr. B. S. Butler of the U. S. Geological Survey has acquainted us of an interesting occurrence of this mineral, to which he has given careful study. In the Hornsilver Mine near Frisco, Beaver Co., Utah, wurtzite seems to be undoubtedly a product of secondary sulphide enrichment. The original ore, still fresh in the lower levels, contains galena, pyrite and sphalerite, a little chalcopyrite, and possibly other copper minerals. The upper part of the deposit has been largely oxidized to sulphates, minor quantities of carbonates and other secondary minerals forming also. Octahedral cavities in the rock bear testimony to the former presence of pyrite, which, though plentiful lower down, has now disappeared from the oxidized zone. Below this lies a zone of secondary sulphide enrichment carrying secondary (reprecipitated) chalcocite, covellite, and wurtzite in large quantities, much of the last named precipitated around original sphalerite cores. The chemistry of these processes must have involved first the oxidization of the sulphides of zinc, copper, and iron to sulphates, and since the original ore contained pyrite, the oxidized solution must have contained sulphuric acid. As this solution moved downward, the sulphuric acid gradually decomposed the more soluble sulphides of the unoxidized ore with the formation of sulphates and hydrogen sulphide. At greater depths, after the oxygen of the solution was entirely used up and the acid reduced, the sulphides were reprecipitated. The difficultly soluble sulphides of copper would readily precipitate on the more

* At least, it can form only from acid solutions.

easily soluble sulphide of zinc. Of course the sphalerite could not have precipitated wurtzite directly out of the solution since wurtzite should be the more soluble of the two, but when the acid in the solution had become sufficiently neutralized or used up in any way whatever, the hydrogen sulphide present would precipitate the zinc after the less soluble sulphides of copper.

In this instance, therefore, the formation of wurtzite is well explained by our synthetic experiments and it will be interesting to learn whether other occurrences of wurtzite may not be similarly explained. It appears quite possible that wurtzite may often have been taken for sphalerite on account of the general similarity between the two and the lack of careful examination.

The origin of "schalenblende," which seems to consist of alternate layers of the two forms of zinc sulphide, is difficult to explain, but the suggestion is made that some systematic alteration of conditions may have resulted in the periodic neutralization of a slightly acid solution.

II. THE SULPHIDE OF CADMIUM.

So far as present knowledge goes, sulphur forms with cadmium only* the monosulphide, CdS . Schiff† claimed that a pentasulphide was precipitated from solutions of cadmium salts by potassium pentasulphide, but Buchner‡ proved that the precipitate thus formed was merely a mixture of the monosulphide with sulphur. Cadmium sulphide occurs in nature only as the mineral greenockite which crystallizes in the hexagonal system, but at least two other crystalline forms have been reported as laboratory products.§ From several points of view it is of interest to know whether these forms actually exist—especially whether there is one of regular symmetry analogous to sphalerite, the common sulphide of zinc, and a systematic investigation of the question was, therefore, undertaken.

Thermal behavior of Cadmium sulphide.

A sample of amorphous cadmium sulphide was first heated in a current of hydrogen sulphide in the manner previously described in this paper (p. 345). The sulphide was raised to a temperature of about 1000° and held there for two hours. After cooling, it was submitted to a microscopic examination, when it was found to be entirely crystalline. Individuals were

* See Follenius, *Zs. anal. Ch.*, xiii, 411, 1874.

† Liebig's *Ann.*, cxv. 68; *J. B. Ch.*, 1860, 84.

‡ *Chem. Ztg.*, xi, 1087, 1107, 1887.

§ Lorenz, *Ber.*, xxiv, 1501, 1891. Klobukow, *J. pr. Chem.* (2), xxxix, 412, 1887. Beyerinck, *N. J.*, 1897-8, *Beilage Bd. xi*, 432.

naturally not well developed in the mass, though there were some well-formed prisms which had evidently crystallized direct from the vapor. The whole product was identified by its optical properties as greenockite. This mineral has been formed* by others at high temperatures and its volatility has been noted.† Heating and cooling curves were determined on the product crystallized as above, the same apparatus being used. No break was found anywhere from ordinary temperature to 1000° to indicate any physical transformation whatever. These results, however, can not safely be regarded as conclusive, because the effects which accompany definite physical changes are sometimes too small to be thus detected. Furthermore, unstable forms are often capable of existence under certain conditions, while they would not be found under circumstances like those described above.

Lorenz‡ states that he obtained beautiful crystals of cadmium sulphide by vaporizing metallic cadmium in a strong current of hydrogen sulphide. The preparation was examined by Prof. Groth, who found in it simple crystals of greenockite, and also twinned forms in large number, which he regarded as monoclinic. Lorenz accounted for two crystal forms in the same preparation by the supposition that the temperature varied greatly in different parts of the mass. We made two preparations by this method. The largest crystals, which surpassed 20^{mm} in length, were made by heating in a resistance furnace a porcelain tube which enclosed the boat containing the metal. When the boiling point of cadmium was reached the galvanometer indicated a temperature of 780° , which held constant about ten minutes. After heating half an hour longer, during which the hydrogen sulphide was passed in rapidly, the furnace was cooled down. The product so obtained and also a previous one made by heating with an ordinary blast lamp, contained many twinned crystals, as well as simple prisms of greenockite. It would be easy to mistake these forms for monoclinic twins, but a careful study of them by Dr. Merwin (Microscopic Study) has shown conclusively that they are hexagonal, twinned after two different pyramids.

The cadmium which we used in the formation of the sulphide was of known composition; the total impurities were $\text{Pb} = .086$ per cent, $\text{Fe} = .002$ per cent. The sulphide was,

* Deville & Troost obtained it by heating the amorphous sulphide to a white heat in a current of hydrogen; also by heating together CdSO_4 , BaS and CaF_2 in equal quantities; C. R., lii, 920, 1861. Mourlot sublimed cadmium sulphide in the arc furnace; C. R., cxxiii, 54, 1896.

† Biltz states that greenockite begins to sublime about 980° ; Zs. anorg. Ch., lix, 273, 1908.

‡ Loc. cit.

therefore, tested for these impurities only, and then used for a determination of the density. No lead was found, though .02 per cent of residue remained after driving off the volatile acid of the chloride with sulphuric acid. There was also a trace of iron which probably came from the reagents. Nearly 10 g. of material were used in the gravity determination. At 25° the value 4.833 was obtained. After finer crushing, to eliminate possible air bubbles, a second determination gave 4.835, proving that porosity was negligible—a conclusion confirmed by the microscope. From the above value we obtain the density $\frac{\text{mineral at } 25^\circ}{\text{water at } 4^\circ} = 4.820$. The value of this constant given in the text-books depends on meager data and is, doubtless, too high.*

At a much lower temperature, well developed prisms (about 1^{mm} maximum length) were obtained by Schüler's† method—i. e. by heating‡ the amorphous sulphide with a flux consisting of equal parts of potassium carbonate and sulphur.§ These prisms were also hexagonal. They probably dissolve a small percentage from the flux, since Merwin finds $\epsilon_{L_1} = 2.447$ as compared with 2.45 for greenockite prepared by heating the amorphous sulphide in hydrogen sulphide.

Cadmium sulphide from acid solutions.

Failing to get any evidence of the existence of any other sulphide of cadmium than the ordinary greenockite by dry methods, experiments on aqueous solutions were undertaken. When acid solutions of cadmium salts are precipitated by hydrogen sulphide, the product may be either amorphous or crystalline—the result depending on the rapidity of precipitation, the acidity of the solution, its cadmium concentration, temperature, etc., as it is with zinc salts. By the use of the double tube, a device already referred to (p. 355), hydrogen sulphide was generated slowly, and comparatively large prisms (about 0.5^{mm} long) were obtained. The composition of the solution in the inside tube was 2 g. $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O} + 20 \text{ cc. } 30\% \text{H}_2\text{SO}_4$; the outside tube contained 9 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} + 20 \text{ cc. water}$. The duration of the experiment was three days at 180°. The crystals were undoubtedly greenockite, though the index of refraction, ϵ_{L_1} , was slightly lower than that of the purest product, being 2.440 instead of 2.456. This is accounted for

* Thus Dana (Text-book of Mineralogy, 6th ed., 1906) gives 4.9 — 5.0.

† Lieb. Ann., lxxxvii, 40, 1853.

‡ The temperature in one experiment was 365°.

§ Much amorphous residue remained after dissolving out the flux with water, perhaps from a decomposition of a compound of the cadmium and potassium sulphides.

by the probable presence of cadmium sulphate in the crystals, a hypothesis which is in accord with the well known tendency of this substance to occlude salts from the solution in which it is precipitated.

In other experiments carried out in a similar way, the crystals of the product were smaller. When amorphous cadmium sulphide was heated in a sealed tube with 30 per cent sulphuric acid at 200° for two days, the product consisted of spherulitic aggregations of small *doubly refracting prisms*. Again hydrogen sulphide was passed into a boiling solution which contained 1 g. $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ in 50 cc. 30 % H_2SO_4 . After the air had been entirely replaced from the flask, the latter was connected with the hydrogen sulphide generator and allowed to cool. Most of the product crystallized during the cooling. It consisted of spheroidal lumps of amorphous material shot through with *doubly refracting needles*. The crystals of the two last-named products showed *parallel extinction* though they were too small for a determination of the refractive index.

We also prepared crystalline cadmium sulphide by the method of Geitner,* which consists in heating the metal with sulphurous acid in sealed tubes. Cadmium chips were sealed up in a tube of Jena combustion glass with a solution of sulphurous acid, saturated at room temperature. The tube was heated to 200° for two days. The crystals of the product were of such size that it was possible to determine the crystal system. They were *hexagonal*.

Cadmium sulphide from alkaline solutions.

If cadmium sulphide behaves like zinc sulphide, its closest analogue, we should expect a different product to crystallize from alkaline solutions, perhaps a regular form similar to sphalerite. In the first place we repeated Stanek's† experiments—heating the amorphous sulphide with excess of colorless ammonium sulphide in a sealed tube to 150° – 200° . We used in our experiment $1/2$ g. $\text{CdSO}_4 \cdot 8/3 \text{H}_2\text{O}$ with excess of colorless ammonium sulphide, prepared from concentrated ammonia. The sealed tube was heated three days at 200° . Microscopic examination of the product showed that it was all crystallized in *doubly refracting needles showing parallel extinction*. In a repetition of this experiment, larger crystals were obtained; they were well-formed *hemimorphic* prisms, undoubtedly greenockite. On the other hand, no crystalline product was obtained with sodium or potassium sulphides. Orange-colored sulphide of cadmium remained unchanged, when heated at 200° for two days with dilute solutions of potassium (3.5 per cent) or sodium

* Liebig's Ann., cxxix, 350. J. B. Ch., 1864, 140.

† Zs. anorg. Ch., xvii, 1898.

(2 per cent) sulphide. Concentrated solutions of these reagents change the orange-colored sulphide to a bright yellow color. This is caused by a subdivision of the particles of the latter (see p. 391). Thus 0.1 g. $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ was dissolved in a little water and enough sodium sulphide was added to make a solution of about 13 per cent concentration. The mixture was then poured into a platinum tube and the latter was set inside of a larger glass tube, which was then sealed. After 8 days at a maximum temperature of 260° , no crystals had been formed. In a similar way about half a gram of the amorphous cadmium sulphide was heated with an excess of 20 per cent sodium sulphide for 7 days at a maximum temperature of 275° . Again no crystals were obtained. We may therefore infer that cadmium sulphide is more soluble in ammonium sulphide than it is in the alkali sulphides, while with zinc sulphide the opposite is true.

We conclude from the foregoing that no regular form of cadmium sulphide is obtained from alkali sulphide solutions, and that the analogy with zinc does not hold.

Effect of Sodium thiosulphate on soluble Cadmium salts.

The crystal form of the precipitate thrown down by sodium thiosulphate from cadmium sulphate solutions was also investigated. The principal reaction with excess of reagent is the same as that with zinc, mercuric and ferrous salts. There is evidently a secondary reaction producing a little sulphurous acid, and reducing the amount of thiosulphate consumed. The sulphide also sticks obstinately to the glass and occludes a little sulphate, making it difficult to obtain quantitative results, though the latter are good enough to prove that the chief reaction *with excess* of thiosulphate is $4\text{Na}_2\text{S}_2\text{O}_3 + \text{CdSO}_4 = 4\text{Na}_2\text{SO}_4 + \text{CdS} + 4\text{S}$. The following data were obtained in sealed tubes at 100° :

TABLE VIII.
Action of $\text{Na}_2\text{S}_2\text{O}_3$ on CdSO_4 .

	Taken			$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$		CdS + S		CdS	
	$\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	H_2O	Used up	Cal.	found	Cal.	found	Cal.
1	1.000g	5.006g	75-1000cc	3.44	3.87	0.98	1.06	0.54	0.56
2	"	"	"	3.56	3.87	----	----	----	----

A product obtained under the same conditions was examined by the microscope. It was too fine to identify; it consisted of small orange-colored doubly refracting crystals. Such properties as could be determined, therefore, agreed with greenockite.

Explanation of color differences in Cadmium sulphide.

Cadmium sulphide is a well-known artist's color, and varies from lemon-yellow to orange-red according to the method by which it is prepared: Follenius,* having proved that there was but one sulphide of cadmium, came to the conclusion that these different tints were due to the variable quantity of occluded impurities which he found the sulphide contained. Buchner† appears to have disproved this. He gives no quantitative data, but asserts that he has examined many hundred preparations and finds that sulphide of different tints may contain the same quantity of impurities while variable amounts of the latter occur in sulphide of the same tint. Buchner describes two different "forms" of cadmium sulphide, the methods of preparing which are not very clearly given, one of which is lemon-yellow, the other "almost as red as minium." Most products, he says, are mixtures of these two forms. Solutions containing little free acid give with hydrogen sulphide a yellow precipitate which becomes orange when it is heated in acid or alkaline solutions. Buchner asserts that he has never found crystals in any preparation of cadmium sulphide. He regards the orange or " β -form" a polymer of the yellow or " α -form" because it always has a higher density. Later Klobukow obtained from Buchner a large number of products and sought to prove whether their difference in color was due to chemical or physical differences. He confirmed Buchner's statements regarding the density of the two supposed modifications. At 17° – 17.5° , after drying at 105° – 107° , the yellow form gave specific gravities varying from 3.906 to 3.927, while the orange form showed specific gravities which varied from 4.492 to 4.513. These and other preparations were also examined microscopically by Prof. Haushofer. He found them generally doubly refracting, but makes no specific statements regarding extinction angles, indices of refraction or other constants, except that the crystals of the " α -form" were not crystallographically well determined. He regarded the " α -form" as identical with greenockite, while the " β -products" probably contained both regular and monoclinic forms.

Our experiments confirm Buchner's experimental observations in almost all respects, but a microscopic examination of products of many different hues, made in several ways, prove that the differences in color are primarily dependent on the

* Loc. cit.

† Loc. cit.

amorphous or crystalline nature of the substance and on its state of division; and in a minor degree on the nature of its surface, etc.

1st. The *crystals* vary from clear yellow, in tufts of hair-like needles, to brownish yellow in the larger ones, but *the powder of all specimens is orange*. Still, there is no doubt that all are the same crystalline form; the different colors are due to the relative amounts of light transmitted and reflected.

2d. Amorphous cadmium sulphide shows all tints from lemon yellow to orange red. Light yellow products are obtained by precipitating cold solutions of low cadmium concentration by hydrogen sulphide, or by precipitating cadmium solutions with the alkali sulphides. The microscope shows that the globules of these amorphous precipitates are all very small and of similar magnitude.

The deep orange precipitates are obtained by precipitating hot acid cadmium solutions with hydrogen sulphide, or by long boiling of cadmium solutions with excess of thiosulphate. When the first method is used, a high concentration of acid gives a deeper-colored product. The orange amorphous cadmium sulphide is made up of larger aggregates than the yellow—sometimes fifty times as great in diameter. (See microscopic part.) A very illuminating experiment on this subject was carried out as follows: To about 200 cc. water 4 g. NaCl, 10 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 2 g. $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ were added. The solution was heated to boiling and kept in ebullition for some hours, hot water being added from time to time. Precipitation began almost at once. After about an hour a little of the lemon yellow product was removed and examined microscopically. The particles were too small to measure. After $2\frac{1}{2}$ hours the product had much increased in quantity, but was still light yellow. The microscope showed that it was made up of clear globules about $\cdot 001^{\text{mm}}$ in diameter. Gradually the precipitate grew denser and darker in color until after 4 or 5 hours it had all settled to the bottom, and showed a bright orange color. This product contained particles of all sizes up to $\cdot 05^{\text{mm}}$ in diameter.

Another piece of evidence in point is this: the light yellow precipitate formed by the action of ammonium sulphide on a cadmium salt retains the same color after the system has been heated, though the product is now all crystalline greenockite. When, however, the latter is ground in a mortar it becomes orange in color. This proves quite conclusively that the difference in color has no connection with another crystalline form. Klobukow gives a much lower density for the yellow products than for the orange, viz., 3.906 – 3.927 against 4.492 – 4.513. This looks like a specific constant, but it must

be remembered that the density of the products would be changed a great deal by varying intermixtures of crystalline sulphide which Haushofer says was present in these products, and also by occluded salts. Furthermore, in our experience very fine powders are apt to give densities several per cent lower than the same substance in a coarser form.

In view of all the facts Buchner's hypothesis of polymerization appears untenable.

Change in color of Cadmium sulphide with rising temperature.—When cadmium sulphide is heated, its color becomes progressively darker, until at the full heat of the Bunsen burner, 800° – 900° , it is dark red. On cooling, however, it regains its former color. This behavior is entirely similar in character to that of mercuric sulphide (see p. 379), and like that of the latter is to be attributed to a varying absorption of light with rising temperature rather than to a reversible transformation, for the change is perfectly gradual. To avoid the formation of oxide, the experiments were made in evacuated tubes of Jena combustion glass. At 450° the amorphous sulphide had entirely crystallized in two days' time.

Only one sulphide of Cadmium.—We find no convincing evidence either in the literature or in our own experiments that cadmium sulphide crystallizes in more than one form. We have crystallized it by every method we could devise and have obtained greenockite in every case, or where in some instances the crystals were too small to identify, what properties could be determined agreed with greenockite.

III. THE SULPHIDES OF MERCURY.

There are two sulphides of mercury occurring naturally, the well-known cinnabar and the much rarer metacinnabar. In addition to these there is another form, probably hexagonal, not known in nature. All have the same composition, HgS .

Cinnabar, $\sigma\text{-HgS}$, is readily formed in the wet way by the action of the soluble alkali sulphides on the amorphous black sulphide of mercury. The most satisfactory preparation method is to heat the latter in a sealed tube at 100° with concentrated ammonium sulphide. In a short time the product changes to a vermilion color, but it is best to continue the action for 24 hours to insure a thorough transformation.

The amorphous mercuric sulphide which we used in our work was carefully analyzed. It contained no other metal than mercury except a trace of iron. A small quantity of free mercury and some chlorine, probably in the form of $\text{HgCl}_2 \cdot 2\text{HgS}$,

were present, but both the latter are removed by ammonium sulphide.*

Any form of mercuric sulphide dissolves readily in concentrated solutions of sodium (20% Na_2S , and 35% K_2S were actually used) or potassium sulphide. If the sulphide of mercury is kept in excess, the product is much darker than the vermilion powder formed by ammonium sulphide. The difference is solely one of division. The darker product consists of crystals easily recognized by the naked eye. These, when ground in the mortar, are scarcely distinguishable from the vermilion powder made from ammonium sulphide, while the optical properties as determined by the microscope are identical. The alkali sulphides form with mercuric sulphide two compounds $\text{HgS} \cdot 2\text{M}_2\text{S}$ and $\text{HgS} \cdot \text{M}_2\text{S}$. The latter, we may mention in passing, is easily formed in long hair-like needles of dark green color, when the alkali sulphide solution is evaporated. Individually developed crystals of cinnabar are formed by the solvent action of dilute solutions of the alkali sulphides on mercuric sulphide. The black amorphous sulphide is always the first product when mercuric salts are precipitated by alkali sulphides, but on digestion with the latter at 100° , it gradually passes into cinnabar. Much interest attaches to the fact that *cinnabar only is obtained from these alkaline solutions*. (See p. 380.) Numerous experiments were made with mercuric chloride and dilute solutions of sodium or potassium sulphide or polysulphide between 100° and 200° . The experiments were made in sealed tubes and were continued several days. Many of the experiments were discontinued before the amorphous black sulphide was all crystallized, but *metacinnabar was never observed and cinnabar was always found*.

Effect of sublimation on Vermilion, HgS .

When the red powder which is formed by the action of ammonium sulphide is sublimed in an evacuated glass tube, the sublimate is quite black. If the layer on the walls of the tube is very thin, i. e. was cooled with sufficient rapidity, it is *entirely* black, but in thick layers the product is practically all coarsely crystallized cinnabar coated with a thin layer of the black sulphide. Whether this coating is amorphous or crystalline metacinnabar, it is impossible to say. Ground in a mortar the product is liver-colored like some ores of mercury. If, now, the ground sample is treated with a few cubic centi-

* The original amorphous sulphide always left a small residue of metallic mercury when the sulphide was dissolved by sodium or potassium sulphide solution, while the red product formed from it showed none when treated in the same manner. The chlorine in the original product volatilized as mercuric chloride when heated in an evacuated glass tube.

meters of strong sodium sulphide solution and allowed to stand for a short time, the black material is completely removed. After the addition of a little water the product is filtered and then washed with more and more dilute sodium sulphide solution, so as to prevent the precipitation of the dissolved HgS , and finally with water. This treatment would also remove free sulphur in case any had formed by dissociation of some HgS , during the process of sublimation. The product is now digested with warm dilute nitric acid to remove any free mercury,* washed with water, alcohol and ether and thoroughly dried in a vacuum desiccator containing sulphuric acid. This product showed, under the microscope, all the properties of cinnabar in much larger crystals than the original powder. Table IX shows the specific gravities of various preparations of cinnabar before and after sublimation.

TABLE IX.
Specific gravities of cinnabar at 25°.

Sublimed and purified.		Vermilion powder.	
Prep. I.	Prep. II.	Prep. I.	Prep. II.
8.200	8.198	8.191	8.186
8.198		8.190	
		8.188	
		8.188	
		8.187	

Careful experiments have shown that the vermilion powder contains a little carbonaceous matter as well as about 0.02 per cent of sulphide of iron. The sublimed product is purer and its constants are to be regarded as more reliable.

The density of the pure cinnabar, $\frac{\text{Mineral at } 25^\circ}{\text{Water at } 4^\circ}$ would be therefore 8.176. The lower refractive index directly measured is, $n_{\text{Li}} = 2.85$. The double refraction is 0.35, making the higher index $n_{\text{Li}} = 3.20$. (See microscopic part.)

The behavior of mercuric salts with soluble thiosulphates.

Before going further it will be well to explain the interesting chemical behavior of mercuric salts with soluble thiosulphates, which is somewhat complicated. Three solid phases may be obtained from such solutions which contain from 0–25 per cent by weight of total salts. For the purposes of this investigation it was thought unwise to carry the concentrations farther. It was found that the chemical reactions depended entirely on the ratios between the salts, while the phase which separated was also dependent on the degree of dilution.

* A very high specific gravity (8.7) of one product prepared without digesting with nitric acid was strong indication of the presence of mercury.

The facts may be clearly presented by means of a triangular diagram, from an inspection of which we can see the relation of the solid phases to the composition of the solutions out of which they crystallize, but it must be understood that the phases do not represent equilibrium relations, though the relations are constant. The diagram (fig. 5) refers only to 10

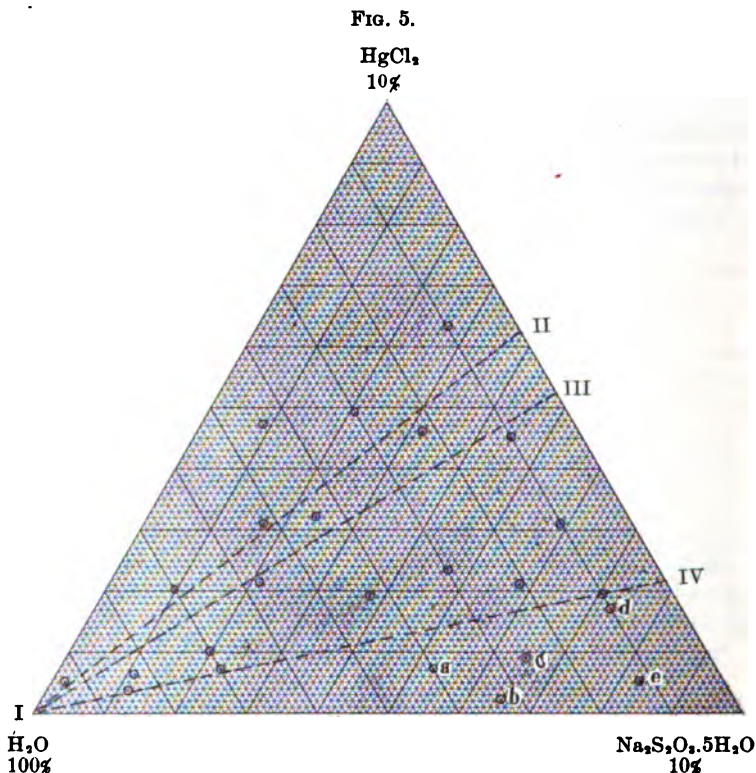


FIG. 5. The action of sodium thiosulphate on mercuric chloride in solutions of varying composition.

per cent solutions. All the solutions plotted contain a constant quantity of sodium chloride (2 g. per 100^{cc}), it having been found that the decomposition of sodium mercuric chloride proceeds much more slowly than that of mercuric chloride and better crystals appear to be obtained by the use of it.

1. All solutions lying in the field above the line I,II precipitate white mercuric chlorosulphide, $\text{HgCl}_2 \cdot 2\text{HgS}$. It will be observed that the line I,II includes all solutions in which the ratio of HgCl_2 to $\text{Na}_2\text{S}_2\text{O}_3$ is as 3 mol : 2 mol while all solu-

tions in the field alluded to contain more mercuric chloride than this ratio. The chemical reaction which will be proved below is :



2. All solutions lying in the field included between I,II and I,III precipitate mixtures of $\text{HgCl}_2 \cdot 2\text{HgS}$ and black HgS , apparently amorphous. All solutions on the line I,III contain HgCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ in the ratio 1 mol : 1 mol. The chemical reaction is $\text{H}_2\text{O} + \text{Na}_2\text{S}_2\text{O}_3 + \text{HgCl}_2 = 2\text{NaCl} + \text{H}_2\text{SO}_4 + \text{HgS}$ (black).

3. All solutions lying between the lines I,III and I,IV precipitate, *in the beginning*, black HgS , though later a red precipitate may be obtained.

4. The line I,IV includes all solutions in which the ratio of HgCl_2 to $\text{Na}_2\text{S}_2\text{O}_3$ is 1 mol : 4 mol. The principal reaction is $\text{HgCl}_2 + 4\text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaCl} + 3\text{Na}_2\text{SO}_4 + 4\text{S} + \text{HgS}$. The mercuric sulphide precipitated here is, in the beginning, a deep red modification which the microscope shows is not cinnabar but a new form, appearing transparent and orange-colored under the microscope and having lower indices of refraction than cinnabar. It should be stated here that the precipitation of this phase continues until the dilution of the supernatant liquid has fallen to about 1 per cent of mercuric chloride, when the black form in crystalline condition begins to come down with it.

Proof of the above reactions.—1. The reaction $3\text{HgCl}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{H}_2\text{O} = \text{HgCl}_2 \cdot 2\text{HgS} + 4\text{NaCl} + 2\text{H}_2\text{SO}_4$. A solution containing 2.0 g. NaCl , 1.64 g. HgCl_2 , and 1.000 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 100 to 200° water was boiled for a short time and filtered. No gas escaped during the process. The curdy yellowish precipitate was carefully washed, and the filtrate and washings were diluted to 250°. This solution was free from mercury, gave a strong acid reaction with litmus and a decided reaction for sulphate with barium chloride.

0.2011 g. pure dry sodium carbonate required of this solution 120.6° for neutralization, using methyl orange as an indicator. 0.386 g. H_2SO_4 found. 0.394 g. H_2SO_4 cal. from the above equation.* In a second experiment 20 g. NaCl , 1.65 g. HgCl_2 , and 1.000 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in about 200° water were boiled and filtered as before.† The filtrate was diluted to 500°. It contained no mercury, no thiosulphate and was strongly acid as before. No sulphur dioxide was evolved during the reaction. 0.3006 g. Na_2CO_3 required for neutralization 348.5° solution, using as indicator phenol phthalein at boiling temperature. Total H_2SO_4 found 0.3991. Cal. from equation .3955. Thor-

* It will be remembered that the thiosulphate has the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

† It may be the slight excess of mercury was absorbed by the precipitate.

oughly washed precipitates made in the above way were dried and analyzed. In all of them a small excess only of mercuric chloride was used, since a large excess gave finely divided precipitates difficult to wash.

	Found.			Cal. for $\text{HgCl}_2 \cdot 2 \text{HgS}$.
	1.	2.	3.	
Hg	81.51	----	----	81.58
Cl	----	9.37	----	9.41
H_2O	.44	----	.48	----

2. The reaction $\text{H}_2\text{O} + \text{HgCl}_2 + \text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaCl} + \text{HgS} + \text{H}_2\text{SO}_4$. 1.000 g. HgCl_2 and 2.0 g. NaCl were dissolved in water and added to a solution of 0.920 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, the total volume after all was added being 150 $^\circ$. A curdy yellow precipitate was obtained in the cold, probably mercuric thiosulphate, which on boiling turned black. A careful test of the precipitate for chlorine revealed not more than a trace. In a second experiment a solution containing 1.10 g. HgCl_2 , 2.0 g. NaCl and 1.000 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 150 $^\circ$ water was boiled for a short time and filtered. The filtrate and washings were diluted to 250 $^\circ$. The resulting solution contained no mercury but was strongly acid. 0.2024 g. pure dry Na_2CO_3 required 119.4 $^\circ$ of solution for neutralization, using as indicator phenol phthalein at boiling temperature. Total H_2SO_4 found = 0.3921. Cal. from the equation 0.3951. In a duplicate experiment a solution identical with the first was prepared, washed and filtered. The filtrate and washings were diluted to 250 $^\circ$ as before. 0.2029 g. pure dry Na_2CO_3 required 119.5 $^\circ$ solution for complete neutralization. Total H_2SO_4 found = 0.3927. Cal. from the equation 0.3951.

3. The reaction $\text{HgCl}_2 + 4\text{Na}_2\text{S}_2\text{O}_3 = \text{HgS} + 4\text{S} + 2\text{NaCl} + 3\text{Na}_2\text{SO}_4$. This is the principal reaction at 100 $^\circ$ in sealed tubes when the thiosulphate is present in sufficient excess. The solution is generally, however, slightly acid, and when it is boiled in an open vessel considerable sulphur dioxide is evolved. All the mercury is precipitated, and in two distinct layers. The bottom layer, which of course, precipitated first, is bright red and consists of the new hexagonal mercuric sulphide which we will call β' - HgS ,* the upper layer consists of a mixture of this form with metacinnabar, α' - HgS . The total precipitate when mixed has a puce color almost exactly like lead peroxide. It contains the α' - HgS and β' - HgS in approximately equal quantities, as was estimated by matching the color with various mixtures of the pure substances.

* We will use the symbol σ to designate the stable form and for monotropic forms the symbols α' , β' to distinguish them from enantiotropic forms, for which the unaccented letters are commonly used.

As evidence of the above reaction we give the following data:

TABLE X.

Action of HgCl_2 on a large excess of $\text{Na}_2\text{S}_2\text{O}_3$.

	HgCl_2 taken	$\text{Na}_2\text{S}_2\text{O}_3$ $5\text{H}_2\text{O}$ taken	NaCl taken	H_2O taken	$\text{Na}_2\text{S}_2\text{O}_3$ $5\text{H}_2\text{O}$ used	$\text{Na}_2\text{S}_2\text{O}_3$ $5\text{H}_2\text{O}$ Cal.	$\text{HgS} + \text{S}$ found	$\text{HgS} + \text{S}$ Cal.	HgS found	HgS Cal.
1.	1.000g	5.000g	2.0g	75°	3.66	3.66	1.32	1.32	.86	.85
2.	1.000g	5.000g	2.0g	75°	3.56	3.66	1.29	1.32	.82	.85

The data were obtained in the manner described on p. 352, i. e., the excess of thiosulphate was obtained by titrating an aliquot part of the filtrate with iodine; the total weight of the precipitate, washed with alcohol and dried, was then taken, and finally the weight of the sulphide was found after extracting the precipitate with carbon disulphide, washing out the excess with ether, and drying.

Metacinnabar, α' - HgS . The metacinnabar of nature, when pure, is entirely black and crystalline and is generally regarded as an isometric mineral, though crystallographic data are meager. We have obtained black crystalline mercuric sulphide by only one method, viz., by the action of an excess of sodium thiosulphate on sodium mercuric chloride in dilute solution. By reference to the previous pages (pp. 371-372) it will be seen that moderately concentrated solutions (10%-25%) of total salts containing the substances in the ratio $\text{HgCl}_2 : 4\text{Na}_2\text{S}_2\text{O}_3$ give first a red precipitate, which continues to form until the concentration of the mercuric chloride is approximately 1 per cent, when the black crystalline sulphide separates with the red. The solutions *a*, *b*, *c*, *d*, *e* (fig. 5) precipitated a mixture of the two forms from the outset. The formation of the red modification may be entirely inhibited, however, by the addition of sulphuric acid to the solution before boiling. In six different experiments where the concentration of the mercuric chloride remained constant, 1 g. : 700° H_2O , and the thiosulphate varied from 2 g. to 20 g., the addition of 4 drops 30% H_2SO_4 entirely prevented the formation of the transparent red sulphide. This was proved by microscopic examination of the products. On the other hand, if the acid was omitted, all the other conditions remaining constant, a large quantity of the red form (β' - HgS) was intermixed. For the preparation of the black α' - HgS in

portions large enough for a specific gravity determination, we used the following solution: 6 g. HgCl_2 ; 60 g. NaCl ; 12 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 4l. of water. 10% 30 per cent sulphuric acid was added and the solution boiled till precipitation was complete. More than a proportional quantity of acid was thus required for the larger volume of solution. The precipitate, after thorough washing, was dried with alcohol and ether; then the sulphur was removed by repeated digestion with carbon disulphide, washed with ether, and dried by heating in vacuo to 250° . It contained only a trace of occluded salt. A weighed portion dissolved in aqua regia and changed to chloride with excess of hydrochloric acid was precipitated with hydrogen sulphide. The filtrate was evaporated to dryness and finally heated to redness in a tarred platinum dish and weighed. Three-tenths of a milligram of sodium sulphate in one gram substance = 0.03 per cent was thus obtained. Of course this does not prove the original form of the sodium to have been sulphate, though it probably was. The sulphide was tested for water by heating in an atmosphere of carbon dioxide, till it was largely volatilized, the water being absorbed by calcium chloride. Of course precautions were taken to guard against driving the sulphide vapor over into the absorption tube, and when the apparatus was cold, the carbon dioxide was removed by dry air. No water was found. Under the microscope the product was apparently all crystalline, though it was impossible to say that there was no intermixture of amorphous sulphide.

The slow precipitation of mercuric sulphate or chloride in strongly acid solution by hydrogen sulphide was also tried for the preparation of this form. The device referred to on p. 355 was used for the purpose. The products obtained in this way showed no crystal faces, and being opaque it was impossible to say whether they were crystalline or not. Similar products were also obtained by the action of sulphur and sulphuric acid on metallic mercury in closed tubes containing an atmosphere of hydrogen sulphide. At high temperatures, 200° and 300° , respectively, some cinnabar was obtained by both the last two methods.

Properties of α' -HgS. The opacity of the black mercuric sulphide made optical tests on it impossible. The attempt to prepare measurable crystals of it was futile and therefore our product could not be certainly identified with metacinnabar. The following facts, however, make the identity highly probable. Both minerals are entirely black when pure, even in a powdered condition. Natural metacinnabar is regarded as tismetric; the laboratory product was obtained from thiosulphate solutions in the form of bars crossed at right angles like the principal axes of a cube, suggesting skeleton crystals of the

regular system. The specific gravities of several products made in this way at 25° were,

I	II	III	IV	V	Average
7.592	7.586	7.642	7.588	7.568	7.60

The variation in these determinations is, perhaps, to be accounted for by the presence of some amorphous sulphide in varying quantity. The microscope was unable to decide this point.

The best determinations of the specific gravity of the natural mineral are close to 7.7. G. E. Moore,* who first described and named the mineral, said that the specific gravity varied from 7.701 to 7.748 "owing to intermixed cinnabar." Genth and Penfield,† who obtained the number 7.706 on a specimen of metacinnabar from San Joaquin, Orange County, California, say: "Color iron-black, but many pieces show already a change into ordinary cinnabarite both by a good lens and the reddish black powder which some of the particles yield on pulverizing." It is probable, therefore, that these values are somewhat high; on the other hand, it is possible that the values obtained on the laboratory product are somewhat low, since it was impossible to prove that the latter was free from amorphous material. True, Moore calls the mineral amorphous, but no other investigator confirms him. On heating alone or more rapidly with ammonium sulphide or dilute sulphuric acid, the metacinnabar passes over into cinnabar. This is true for both the natural and the synthetic mineral (see p. 377).

β' -HgS. It has already been stated that the precipitation of solutions of sodium mercuric chloride by sodium thiosulphate in the proportion $\text{HgCl}_2 : 4\text{Na}_2\text{S}_2\text{O}_3$, yields a beautiful red sulphide differing from cinnabar. If the product is to be free from α' -HgS, it should be filtered before precipitation is complete. For this reason it is wise to begin with pretty concentrated solutions, 10 to 25 per cent of total salts, and interrupt the operation while the product is still bright red. It has been found by actual test that the addition of a fraction of 1 per cent of black HgS to the *first precipitate which forms* (the two being thoroughly mixed in a dry condition), can readily be detected by the eye. A microscopic examination in this case was futile. Judging by the color test, the following conditions gave a product about 99.5 per cent pure. Two solutions of 400^{cc} each were prepared; one containing 40 g. NaCl and 34.4 g. HgCl_2 , the other 125.6 g. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. The solutions should be filtered if not perfectly clear, and the sodium mercuric chloride solution is then added gradually, with

* This Journal, iii, 36, 1872.

† Ibid., xlv, 383, 1892.

constant mixing, to the thiosulphate solution. The mixed solution should not contain a trace of precipitate. The product is now brought as rapidly as possible to boiling. After about 12 minutes the precipitate is rapidly filtered on a hot water filter and washed thoroughly with hot water. The temperature of the solution should not be allowed to fall materially during the process. In that case a further precipitate containing some black HgS is formed, as may be seen by the color. When the filtrate has reached room temperature, the further precipitation becomes very slow. If now the supernatant liquid is raised again to boiling, the β' - HgS is again formed. After the precipitate has been dried by alcohol and ether, the free sulphur is removed by carbon disulphide. That the substance is really a sulphide of mercury will be seen from the following analysis :

HgS	=	98.49
Cl	=	.10
Na_2SO_4	=	.23
H_2O	=	1.14
		<hr/>
		99.96

A weighed portion of the substance was dissolved in caustic alkali, and the solution treated for a short time with hydrogen sulphide. A slight excess of dilute sulphuric acid was then added, and finally a slight excess of ammonia. The mercuric sulphide was then collected, freed from sulphur, and weighed according to Treadwell.*

The water and sodium sulphate were determined by the methods described for the α' -compound. The chlorine was doubtless present as sodium chloride, and the remainder of the sodium was probably in the form of sodium sulphate. If we calculate the chlorine and the sodium in this way it would change the above results only a trifle. The greater quantity of impurity found here than in the α' - HgS is due, no doubt, to the higher concentration of salts in the solution which one must use in order to obtain the β' -form. The determinations of density and refractive indices were made on preparations which had been heated to 250° in vacuo for some hours. Determinations of the water and sodium as sulphate in two of them were as follows :

I		II	
H_2O	Na_2SO_4	H_2O	Na_2SO_4
0.37 & 0.46	0.49	----	0.33%

These powders were apparently homogeneous as observed by the microscope, but they were quite fine and somewhat vari-

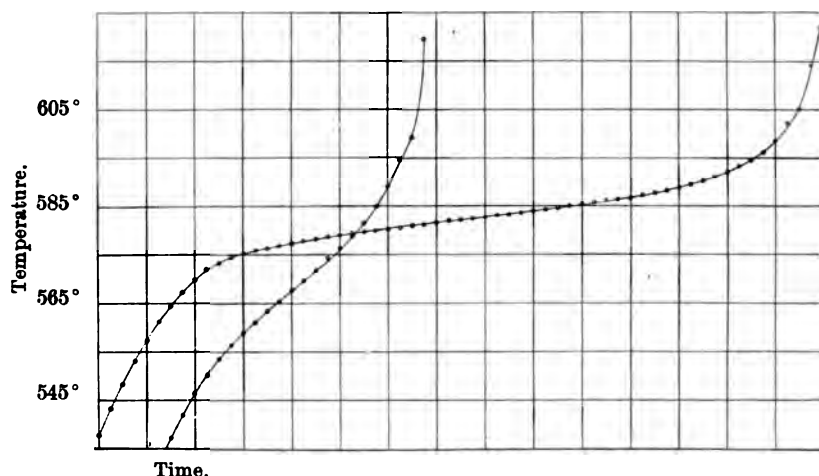
* Quantitative Analysis, translation by Hall, p. 135.

able in specific gravity. The following are the determinations of this property at 25°:

I	II	III	IV	Average
7.221	7.215	7.179	7.199	7.20

The refractive indices in lithium light were found to be 2.58 and 2.82 (Merwin). There can be no doubt that this is a new form of mercuric sulphide with properties quite different from

FIG. 6.

FIG. 6. Sublimation curves of σ -HgS.

cinnabar, though the color of the powder is not to be distinguished from ordinary vermilion.

Relation of the mercuric sulphides to one another.

Like zinc and cadmium sulphides, mercuric sulphide volatilizes without melting at atmospheric pressure. The pressure reaches one atmosphere at about 580°, as may be seen from the curves in fig. 6. In these experiments the sulphide was heated in an atmosphere of hydrogen sulphide. Cinnabar is the stable form over the whole temperature range up to the volatilization point. That the other two forms are both monotropic is proved by the following facts. At 100° both α' -HgS and β' -HgS are changed into cinnabar with ammonium sulphide solution, while at 200° the same change takes place very slowly in sealed tubes with 30 per cent sulphuric acid. At 400°, 450°, 500°, and 550°, both are transformed into cinnabar when heated alone in evacuated glass tubes. The heating was done in a stirred nitrate bath. Table XI shows the results.

TABLE XI. Thermal behavior of mercuric sulphide.

σ -HgS-Cinnabar				α' -HgS-Metacinnabar				β -HgS			
Temperature	Time	Other conditions	Result	Temperature	Time	Other conditions	Result	Temperature	Time	Other conditions	Result
100°	1d	with $(\text{NH}_4)_2\text{S}$	unchanged	100°	--	with $(\text{NH}_4)_2\text{S}$	all changed to cinnabar	100°	1½d	with $(\text{NH}_4)_2\text{S}$	Apparently all changed to cinnabar
---	--	----	----	200°	2d	"	95% changed to cinnabar	200°	--	with 30% H_2SO_4	Slow change to cinnabar
---	--	----	----	200°	4½d	with 30% H_2SO_4	about 10% changed to cinnabar	--	--	----	----
400°	5d	Heated alone in vacuo	< 1% α' -HgS	400°	5d	Heated alone in vacuo	small percentage changed to cinnabar	400°	5d	Heated alone in vacuo	Had the color of a mixture of 35% α' -HgS + 65% cinnabar
450°	5d	"	about 1% α' -HgS	450°	5d	"	95% changed to cinnabar	450°	5d	"	Had the color of a mixture of 15% α' -HgS + 85% cinnabar
500°	3d	"	< 1% α' -HgS	500°	3d	"	More than 99% changed to cinnabar	500°	3d	"	More than 99% changed to cinnabar
---	--	----	----	570°	3d	"	More than 99% changed to cinnabar	--	--	----	----

The thermal behavior of these substances is confusing. In the first place, cinnabar turns black as the temperature rises. This is not due to any transformation, but merely to a variation in the absorption of light with changing temperature, for after it has been heated to 325° for many hours, cinnabar quickly regains its color on cooling. If, however, the temperature is carried to 445° , or perhaps to a lower point, the color remains permanently black. This was first interpreted to mean a transformation into metacinnabar, but a microscopic examination failed to disclose anything but cinnabar, while by grinding in a mortar the black color was found to be due merely to a thin coating. By matching the tint of a ground sample of heated cinnabar with a ground mixture of the red and black sulphides, the former was found to contain 1 per cent or less of the black sulphide. The same final product was obtained whatever form of mercuric sulphide was heated, provided the temperature was as high as 500° and no further change was found on heating to 550° . This is difficult to explain satisfactorily. Possibly the coating is due to a condensation of the vapor to the black form. The volume of the tubes was about 0.5^{cc} and the weight of the sulphide taken was half a gram. On the assumption that the tubes were filled with undissociated vapor

at one atmosphere, they would have contained $\frac{116 \times .09^{\text{mm}}}{2} = 5.2^{\text{mm}}$

of sulphide vapor, and if this were all condensed on the surface of the sulphide, the mixture would have contained 1 per cent of black sulphide. Apparently little or none condensed on the glass at 500° . Even if the vapor pressure were only half an atmosphere, the results would still be of the right order of magnitude. The results on the β' -HgS, while conclusive, regarding the relation between it and cinnabar, do not settle the relative stability of the two unstable forms. With ammonium sulphide the β' -HgS appears to be transformed more slowly than the α' -form, though it is very difficult to detect small grains of cinnabar in a matrix of the former. Again, if we were to judge from the behavior of the β' -HgS when heated in evacuated tubes we might conclude that it passed through the α' -form in its transformation to cinnabar. (See Table XI.) This would make the β' -form the least stable which might be expected from the fact that it is not found in nature. However, the *apparently* large percentage of the black sulphide in the β' -HgS during the early stages of its transformation, may be nothing more than a surface coating on the numerous little grains, which in grinding still remain black because they escape the crushing action of the pestle. At the end of the transformation the β' -HgS has always changed into comparatively large cinnabar crystals in which, of course, the surface is greatly reduced.

The black coating should be thicker here if our explanation is correct, but the grinding process might well give a powder of a redder hue. We found, in accord with this supposition, that a very pure vermilion powder (unsublimed cinnabar) also gave, on heating, a product which was considerably darker after it was ground than a product formed by heating coarser cinnabar.

Whether our explanation be correct or not, it remains certain that metacinnabar and the new β' -HgS are both monotropic forms, while cinnabar is stable.

Genetic conditions of the natural mercuric sulphides.—

The evidence for the geologic view that cinnabar is a product of alkaline solutions is convincing. The close and constant association of the mineral with igneous rocks is significant, while in two well-known localities, Steamboat Springs, Nev.,* and Sulphur Bank, Cal., it seems to be in the process of deposition from alkaline waters at the present day. Posepny† states that in the former locality pyrite is apparently forming with it. Cinnabar is thus undoubtedly a primary mineral. In some cases also it appears to be secondary, since mercurial tetrahedrite oxidizes readily to sulphates, and the descending solution seems to be precipitated as cinnabar on other sulphides at lower levels (Lindgren). Metacinnabar, on the other hand, is regarded as a characteristic secondary mineral. It was found near the surface in the Knoxville district, Cal., and has not been found lower down. A large part of the ore in the Baker Mine and in the upper levels of the Reddington Mine were metacinnabar.‡ Melville§ describes an occurrence of metacinnabar in the New Almaden mines, Santa Clara Co., Cal., where cinnabar and quartz are intimately mixed, while metacinnabar is crystallized on the quartz and is "certainly subsequent to it."

The metacinnabar of Idria, according to Schrauf,|| is far younger than the cinnabar which underlies it and has apparently been formed since the opening of the mines. It occurs here in hemispherical crystal aggregates which suggest to Schrauf that they may have formed by the action of hydrogen sulphide on the globules of metallic mercury which invariably accompany the cinnabar. Schrauf refers here to the experiments of Fleck, which lead him to believe that the metacinnabar formed in the presence of sulphuric acid. It is a noteworthy fact that metacinnabar is commonly associated with marcasite, at least in this country.¶

* W. P. Blake, this Journal (2), xvii, 438, 1854.

† Trans. Min. Eng., p. 228, 1893.

‡ Becker, U. S. G. S. Monograph 13, p. 284.

§ This Journal, xi, 293, 1890.

|| Ueber Metacinnabarite von Idria und dessen Paragenesis. Jahrb. der k. k. geolog. Reichs., xli, p. 379-399, 1891. N. J. Min. 1893, I, referate 465.

¶ Becker, loc. cit., p. 285. Penfield, this Journal, xxix, 452, 1885.

Let us see how these field observations agree with the facts worked out in the laboratory. First, it was found that cinnabar very readily forms at moderately low temperatures (80° - 100°) by the action of dilute alkali sulphide solutions on mercuric salts. Ippen* obtained good crystals at 45° in two months. Never under any conditions have we observed metacinnabar as a product of alkaline solutions.

Black crystalline mercuric sulphide was obtained by the slow precipitation of mercuric salts in acid solutions by the action of soluble thiosulphate. The crystals were not measurable and being opaque could not be positively identified. However there were some indications that they were regular and the identity of the two appears probable. The association of natural metacinnabar with marcasite in the deposits of the western United States is important in this connection because both are regarded by geologists as characteristic secondary minerals, i. e., they were precipitated directly or indirectly by the action of hydrogen sulphide from solutions which had been formed by the oxidation of sulphides near the surface. Such waters would of course contain the metals in the form of sulphates, and also free sulphuric acid if pyrite or any other sulphide of that chemical type were one of the minerals oxidized.

Marcasite has already been formed synthetically from such a solution.†

Chemical and geological relations of deep-seated and surface waters.

The difference in chemical character between "ascending" and "descending" natural waters is well known. As previously stated, our knowledge of the composition of hot springs, and the chemical behavior of common minerals with hot water, lead to the conclusion that the former class must be generally alkaline. Chlorides, bicarbonates and sulphides, especially of the alkali metals, are the characteristic constituents. On the other hand, surface waters in the vicinity of sulphides naturally contain sulphates as oxidation products and are generally acid on account of the frequency of pyrite and marcasite.

Now it is a remarkable fact that the crystalline form of a number of minerals is determined by the acid or alkaline nature of the solutions from which they crystallize. We find three pairs of minerals, pyrite and marcasite (FeS_2), sphalerite and wurtzite (ZnS), and cinnabar and metacinnabar (HgS), one member of which crystallizes from acid solutions only, the other member from alkaline solutions as well. Furthermore it is

* Tsch. Mitt., xiv, 114, 1895.

† Allen, Crenshaw and Johnston, this Journal, xxxiii, 179, 1912.

always the stable form which comes out of the alkaline solutions, while the unstable is obtained only from the acid solutions. The alkaline solutions never give rise to any other than the stable forms, while the acid solutions may give rise to either stable or unstable or both, according to conditions.

This statement is subject to only one qualification, viz., our synthetic black crystalline mercuric sulphide was not positively identified as metacinnabar though it was probably that.

We find in chemical literature one well attested instance of the same rule. Schoch * finds two crystalline oxychlorides of mercury of the composition $\text{HgCl}_2 \cdot 2\text{HgO}$. One of these is red and changes readily into the other, which is black by the action of solutions of alkali carbonate or chloride. The latter form is therefore the stable one, at any rate at low temperatures. The conditions for the formation of these two bodies are essentially identical, except that for the preparation of the red form (*unstable*) the solution must be slightly *acid* while for the black form (*stable*) the solution must be slightly *alkaline*.

The geologic evidence so far as it is at hand seems to agree remarkably well with the above facts. Sphalerite, pyrite and cinnabar are primary minerals; marcasite, metacinnabar and apparently wurtzite are characteristic secondary minerals. As explained above, pyrite, sphalerite and cinnabar may be formed from acid solutions by hydrogen sulphide under certain conditions, consequently we are not surprised to find that they may be secondary as well as primary. There is one fact concerning the occurrence of marcasite and metacinnabar which should be mentioned. Both are sometimes associated with calcite. Whether or not they are paragenetic is a doubtful question. (Lindgren.) If the calcite is not subsequent to the sulphides one would be led to suspect that the original solution must have contained bicarbonates and sulphates. The synthetic work would lead us to expect pyrite from such a solution; still the quantity of free acid required for pure marcasite is very small *at low temperatures* and it may be that the reaction $\text{FeSO}_4 + \text{H}_2\text{S} + \text{S} = \text{FeS}_2 + \text{H}_2\text{SO}_4$ would produce marcasite when the initial concentration of acid was no greater than it is in calcium bicarbonate solutions. It would probably be difficult to verify or refute this by experiment. We are usually obliged to work in the laboratory at higher temperatures and in more concentrated solutions than nature does, in order to get any crystals at all in our limited periods of time.

It will be interesting to see whether other similar cases of polymorphism (or isomerism) exist where the crystal form is determined by the chemical composition of the solution.

* Am. Chem. Jour., xxix, 335, 1903.

It may also well be that the acidity or alkalinity of solutions will be found to determine the *composition* of minerals in certain cases. Thus chemical experience shows that the mineral chalcopyrite CuFeS_2 can be prepared synthetically out of alkaline solutions, while it is a matter of common knowledge that copper is *separated* from iron by hydrogen sulphide in acid solutions.

Geologists regard chalcopyrite in certain occurrences as a secondary mineral. It would be premature to enter upon a chemical discussion of this question at present; the case suffices to illustrate our meaning. Enough work has already been done to show that the difference in chemical character between acid and alkaline solutions, therefore in general between deep-seated and surface solutions, is of vital importance in geochemistry.

IV. MICROSCOPIC STUDY.

Zinc Sulphide.

Amorphous.—If examined immediately after being rapidly precipitated in a pulverulent form, the particles of zinc sulphide are spherical, and have diameters of $\cdot 0002$ to $\cdot 0005^{\text{mm}}$ (2 to 5μ). If the precipitation is slow and the solution is agitated, the particles increase in size, and after standing in contact in the solution may aggregate into clusters or crusts, indicating that they are semi-fluid. In fact, the aggregates when compressed under a cover-glass flatten and break open like a stiff jelly. Though jelly-like, the globules contain very little water. On several occasions such masses after being pressed have been observed to become distinctly doubly refracting (probably crystalline). When formed very slowly in acid solutions without agitation—as in the double tube method—the precipitate is: (1) partly in the form of compact, stratified crusts having a decided double refraction with a parallel to the surface, (2) partly in globules resembling spherulites, and having a parallel to the surface. These crusts and spherules are hardened to the point of being gritty and brittle, yet their refractive indices* are far lower than those of the crystalline forms of zinc sulphide, sphalerite and wurtzite. The results of a large number of measurements are tabulated below.

Pure sphalerite	$n_{\text{Li}} = 2\cdot34$
Pure wurtzite {	$e_{\text{Li}} = 2\cdot35$
{	$w_{\text{Li}} = 2\cdot33$
Amorphous:	
Stiff jelly	$n_{\text{Li}} = 2\cdot18-2\cdot25$
Doubly refracting globules	$n_{\text{Li}} = 2\cdot18-2\cdot24$

* Measured under the microscope in mixtures of amorphous sulphur and selenium. See this Journal, xxxiv, 42, 1912.

Different layers of the hardened amorphous product may have very different refractive indices, perhaps indicating different compositions. The double refraction shown by this amorphous material is probably caused by the strains induced in these nonhomogeneous masses during the process of hardening. At temperatures above 200° these amorphous crusts and spherules soon become partly or wholly crystalline, that is, the resulting product has the refractive index, n_D , of 2.34.

Sphalerite.—The isometric crystalline form of zinc sulphide, sphalerite, was produced from solutions and molten salts in the following typical habits: at about 800° from molten sodium chloride it occurred in the form of distorted dodecahedrons about 0.1^{mm} long; at 350° from a concentrated solution of sodium sulphide, dodecahedrons and tetrahedrons 0.01^{mm} in diameter appeared; at 200° for 11 days in a similar solution, tetrahedrons alone appeared. The refractive index of these crystals for lithium light determined under the microscope was found to be $2.340 \pm .005$. Out of acid solutions definite crystals were not observed, but side by side were seen, in some preparations, spherules and crusts of amorphous zinc sulphide, and similarly shaped masses having no double refraction and the high refractive index. The latter were in some cases covered with minute facets. It appears that an amorphous precipitate is at first formed and that this subsequently crystallizes, probably after having hardened.

Wurtzite.—The hexagonal form, wurtzite, separated from solutions in three extreme habits: (1) Prismatic, hemimorphic crystals strongly striated across the prism faces, and reaching 0.8^{mm} in length, were produced in the double tube in an acid solution after 2 days at about 375° . (2) Crystals, tabular parallel to the base and modified by a different pyramid on each end, occurred with these prisms. (3) Hardened amorphous globules from acid solutions at high temperatures become transformed into coherent masses of very small doubly refracting grains having the mean refractive index of wurtzite. In two cases distinctly radial-fibrous forms, having the characteristics of wurtzite elongated parallel to the prism, were seen. This structure is found in the natural schalenblendes. Experience has shown that these aggregates, immersed in methylene iodide and viewed in ordinary light, may appear entirely isotropic, but mounted in a red mixture of sulphur and selenium having about the same refractive index as the aggregates, they are distinctly doubly refracting in artificial light.

Wurtzite produced by sublimation may appear in slender needles or small stout prisms. Such crystals made from pure zinc sulphide were used for determining the refractive indices under the microscope. The values obtained are as follows:

$\omega_{Li}=2.330$, $\epsilon_{Li}=2.350$, $\omega_{Na}=2.356$, $\epsilon_{Na}=2.378$. An independent measurement of $\epsilon-\omega$ on the prisms gave .019 for Li-light and .020 for Na-light.

Observations on natural Sphalerite and Wurtzite.

Samples from more than twenty different occurrences of natural zinc sulphide minerals were studied optically. With a prism of the light amber-colored sphalerite from Sonora the refractive indices for Na-light and Tl-light were accurately determined on a spectrometer. The values obtained were $2.3688 \pm .0001$ and $2.3990 \pm .0002$. Although this material is the purest natural sphalerite obtainable (containing only 0.22 per cent FeS) the impurity is sufficient to raise the refractive index .0006 for Na-light and .0007 for Tl-light (page 386). The refractive index of pure sphalerite, probably correct within $\pm .0002$, therefore, is $n_{Na} = 2.3682$, $n_{Tl} = 2.3983$.

The dispersion of the Sonora sphalerite was determined from measurements on two prisms, a goniometer and monochromatic illuminator being used. The illuminator was standardized by observations on the following lines: Li, Na, Tl, Sr (blue).

Wave-length	Refractive Index
420	2.517
434	2.493
486	2.436
535	2.399
589	2.369
630	2.353
671	2.340
760	2.320

The effect of dissolved FeS upon the refraction constants of Sphalerite and Wurtzite.—Natural blendes may contain as much as thirty per cent of FeS. Ferriferous blendes are deeply colored, but in very thin flakes they are a clear orange-brown by transmitted light. The blende from Saxony containing 28.2 per cent of FeS absorbs light in gradually increasing amounts from the red end of the spectrum to about 450μ , where it is practically opaque. The wurtzite formed by heating this blende is somewhat lighter in color, but is not distinctly pleochroic in any part of the spectrum. Its average refractive index is very near the refractive index of the blende—was observed to be .005 less—and its double refraction about .02. The mutual optical relations of sphalerite and wurtzite are thus not sensibly altered by the presence of large amounts of FeS.

The absolute values of the refractive indices are greatly increased by FeS. The following table shows the character of

the change for sphalerite. The same values apply to wurtzite also, within the limits of error of the determinations of refractive index—probably about ± 0.005 , due to lack of homogeneity of the blende and to observational errors. The analyses and densities given in the table are by Allen and Crenshaw.

Locality	% FeS (MnS)	d	n_{Li}	n_{Na}	$\frac{n-1}{d}$		$\frac{n-1}{d}$	
					Li	Na	Calculated for FeS.	
							Li	Na
Sonora	0.2	4.090	2.34	2.37	.328	.335		
Spain	8.6	4.023	2.36	2.40	.338	.348	.442	.488
Australia	17.	3.98	2.38	2.43	.346	.358	.436	.471
Saxony	28.2	3.935	2.395	2.47	.355	.373	.427	.470

Assuming that the FeS is dissolved troilite having a density of 4.78, the average refractive index of troilite calculated on the assumption of an additive relation is 3.08 for Li-light and 3.25 for Na-light. However, if the formula $\frac{n^2-1}{n^2+2} \times \frac{1}{d}$ is used in making a similar calculation, the refractive index for Li-light is 4.7. So great a discrepancy indicates that the additive relation of the refraction constants does not hold in this case, or that it is some form of FeS other than troilite that is present in the blende. The latter alternative appears more likely, for mix-crystals of troilite and sphalerite should have intermediate densities, whereas ferri-ferrous blende has a lower density than either of these minerals. A close agreement between the formulas, the observed densities and refractive indices is obtained by assuming that the FeS in the blendes has a density of 3.8 and an average refractive index of 2.8 for Li-light.

Etch-figures and anomalous double refraction.—Triangular etch-figures on a cleavage surface of sphalerite heated in $ZnCl_2$ are sketched in fig. 7, C (p. 389).

Pressure at a point develops double refraction which may become permanent. Fig. 7, D and E, show doubly refracting areas on a cleavage surface around a point at which pressure was applied. The positions of the plate are 45° apart, the lines Cl representing a cleavage direction.

The tooth-like irregularities on fracture surfaces of sphalerite may be distinctly doubly refracting.

Optical and crystallographic relations between Sphalerite and Wurtzite.

The development of double refraction is the only conclusive evidence we have of the change of sphalerite to wurtzite by heating. Inasmuch as the transformation is slow, its progress can be studied. In ferriferous blendes transformation appears to be most rapid, starting usually at a single point in a grain and progressing so that the final product has like orientation throughout. In grains of the purest sphalerites, the wurtzite usually begins developing at more than one point and in different orientations. The structure produced is an intergrowth of lamellæ of wurtzite, each lamella having its principal axis parallel to one of trigonal axes of the sphalerite grain.* It is evident that the strength of the double refraction of a grain thus transformed will be conditioned by the relative development of the four possible sets of lamellæ. J. Beckenkamp† has considered that lamellæ of wurtzite may develop parallel to the trapezohedron of sphalerite. Such lamellæ would outcrop on a cleavage face parallel or normal to cleavages or bisecting the acute angle between cleavage surfaces. All of the outcropping planes would be oblique to cleavage planes. No lamellæ of this sort were seen in the large number of preparations examined during this investigation.

In material furnished by Mr. B. S. Butler, from Beaver Co., Utah, prismatic crystals of wurtzite from a brecciated vein have fragments of sphalerite as nucleii. The traces of the prismatic cleavage of the wurtzite and of the cleavage of the sphalerite appear to be parallel. The wurtzite cleaves parallel to the second order prism.

Beckenkamp has discussed in detail the very close crystallographic relations of sphalerite and wurtzite. With these are now correlated the very slight changes in optical properties, volume, and energy content accompanying the inversion of these minerals.

Cadmium Sulphide.

Amorphous.—The flocculent precipitate of cadmium sulphide is yellow while moist, but it dries to an orange powder which is lumpy and nearly opaque to transmitted light. The lumps can be consolidated by pressure—as by grinding forcibly in a mortar or by compressing on a microscope slide under a cover-glass—into transparent films, some of which become crystalline during and after the compression. The progress of crystallization may be slow, several hours being required for

* Hautefeuille (loc. cit.) recognized this relation.

† *Zs. Kryst.*, xlv, 248, 1908.

the induced radial—or parallel—fibrous structure to attain its apparent maximum double refraction.

The pulverulent precipitate is bright yellow when first formed, and may remain yellow when dry. Conditions which cause aggregation or great increase in size of the particles produce orange-colored powders. The physical characters of powders of various colors are considered in a succeeding section. Amorphous cadmium sulphide has not been observed in a hard, brittle, doubly refracting form like zinc sulphide. When it exhibits double refraction its refractive index approaches the refractive index of greenockite (crystalline CdS).

The tendency to crystallize is much greater in some preparations of amorphous cadmium sulphide than in others. This has been observed particularly when these preparations have been embedded in the mixtures of sulphur and selenium preparatory to obtaining refractive indices. Large clear globules and lumps from dried flocculent precipitates have not crystallized under this condition, but lumpy aggregates of minute globules such as have been formed by heating the latter in strong solutions of sodium sulphide crystallize readily. However, the crystals are oriented at random, and are so minute that only a very strong light reveals their double refraction. On account of the pores in these aggregates their refractive indices could not have been determined were it not for the fact that compressing and moving them about in the viscous mixture causes their surfaces to consolidate into transparent films.*

Crystalline.—By whatever method produced, the crystals of cadmium sulphide as seen in the microscope were prismatic with parallel extinction, elongation c , pure yellow color, and very faint or imperceptible pleochroism. Crystals from the preparations with molten alkali polysulphide were identified as greenockite by goniometric measurements. Three prismatic, hemimorphic crystals about 1^{mm} long furnished the following data: the prism angles varied between 59 and 61° ; 9 angles from the prism to a pyramid varied between $26^\circ 10'$ and $28^\circ 15'$; five of these angles giving the sharpest signals were included between $27^\circ 45'$ and $28^\circ 15'$; the base terminating the end bearing this pyramid was dull; a steeper pyramid with dull faces terminated the other end. The pyramid measured corresponds to 2021 of greenockite.

The observed refractive indices of these prisms for lithium light are $\epsilon=2.447$, $\omega=2.425$. The crystals from cadmium sulphate, slowly precipitated by hydrogen sulphide, gave a

* It was at first thought that these films might have taken up appreciable amounts of the constituents of the mixture, but this is not the case.

value for ϵ of 2.44. Hexagonal crystals of greenockite from sublimed cadmium sulphide have a slightly higher refractive index, $\epsilon=2.456$. The lower refractivity of the crystals formed in contact with salts is attributed to dissolved impurities, for no other optical differences were observed.

The sublimate produced by heating cadmium in hydrogen sulphide contains crystals of greenockite of four very different habits: filaments and needles, stubby prisms, twins after

FIG. 7.

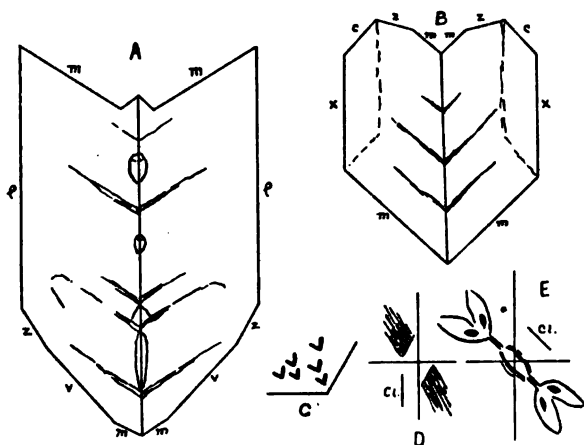


FIG. 7. A, B, Greenockite twin. C, etch figures on sphalerite. D, E, doubly refracting areas on sphalerite.

$10\bar{1}1$, and twins after $20\bar{2}3$. The drawings (fig. 7), made from microscopical studies show the twins. By the elongation of twins like A, feather-like crystals are produced. The angles measured are as follows: $x(10\bar{1}1):c(0001)=43^\circ$; $m(10\bar{1}0):x(10\bar{1}1)=47^\circ$; $m(10\bar{1}0):z(20\bar{2}1)=28^\circ$; $m(10\bar{1}1):v(40\bar{4}1)=15^\circ$; $\rho(20\bar{2}3):v(40\bar{4}1)=43^\circ$; $v(40\bar{4}1):z(20\bar{2}1)=11^\circ$.

The extinction angles measured from the trace of the twinning (and composition) planes are 43° and 32° . The latter angle was measured accurately more than forty times on several twins, with variations less than 1° . The value $32^\circ \pm 10'$ was obtained. For greenockite the calculated angle is $31^\circ 58'$. Poorly developed twins of this type may represent the supposed monoclinic modification of cadmium sulphide.

Optical properties of pure Greenockite.

The chief optical properties of pure greenockite may be inferred from the upper curves of fig. 8. It is uniaxial—positive

for the colors from red to blue-green and negative from blue-green to blue, the wave-length for which it is isotropic being about $523\ \mu\mu$. Above $500\ \mu\mu$ (toward the violet), absorption is so strong that the double refraction has not been measured. By transmitted light, therefore, clear crystals are pure yellow. Plates 0.02mm thick are opaque for all the blue and the violet light that can be obtained from a 20-ampere arc through a monochromatic illuminator. The ordinary ray is more strongly absorbed in the green than the extraordinary ray, for which reason the mineral is pleochroic. In white light the pleochroism is not perceptible in single crystals, but in thin twin crystals it may be seen by contrast in the two parts.

A closer study of the light-absorption of greenockite shows that below (toward the red) wave-length $519\ \mu\mu$ there is very little absorption for ω , and from 517 to 511 it increases to nearly complete opacity. For ϵ absorption begins near 512 and increases similarly to 506 . The change of optical sign is the natural accompaniment of the more rapid increase in refractive index of ω than of ϵ near this region of absorption.

The refractive indices for several different wave-lengths in the red and orange were measured under the microscope. The results are plotted on the diagram. The values for sodium and lithium lights with a probable error of $\pm .003$ are as follows: $\epsilon_{\text{Na}}=2.529$; $\omega_{\text{Na}}=2.506$; $\epsilon_{\text{Li}}=2.456$; $\omega_{\text{Li}}=2.431$. The values used for the curves in the yellow and green are extrapolated on the basis of the absorption, and of the following values for double refraction obtained by measurements on prisms $.03$ to $.04\text{mm}$ thick, in monochromatic light.

671 (Li)	= .025	527	= .006
589 (Na)	= .023	523	= .000
547	= .018	518	= -.006
535 (Tl)	= .013	516	= -.016

Color of Cadmium sulphide.

The color of a substance as seen by reflected light depends upon the character and relative amounts of light reflected directly from external surfaces and indirectly from internal surfaces, that is, after having passed into the substance and reflected out. The quality of the light reflected in each case depends upon the refractive and absorptive powers of the substance, and upon the character (plainness, size, brightness) of the reflecting surfaces.

Greenockite.—This mineral absorbs all the blue and violet and part of the green of the spectrum, and freely transmits the rest. When the greenockite grains seen in mass have diameters of 0.2 to 1.0 or more and are bounded by plane, bright faces, a comparatively large amount of blue light is

directly reflected and a small amount of red, orange, yellow and green are reflected after passing through the surface layer of crystals. The combined effect of all the reflected light is a lustrous, dark, yellow to yellowish-green color, or dark citrene. Similarly, plane-faced bright crystals, but having diameters of $\cdot 01^{\text{mm}}$ or less reflect about the same amount of blue light directly, but they reflect much more of that which has penetrated the surface. The resulting color is a brilliantly pure yellow. Massed crystals of the size of the last but with dull faces have a light yellow-brown or citrene color. A powder consisting of crystalline grains of which the surfaces are mostly bright but not plane, such as is formed by grinding, is invariably a brilliant orange color. In this case there is less direct reflection, and much of the light finally reflected from the interior has penetrated deeper and thus lost more green and yellow than in a powder having plane-faced fragments. Combinations of the physical conditions described cause variations between the extreme colors enumerated.

The colors of dry, *amorphous cadmium sulphide* may be explained in much the same way. The amorphous sulphide, however, absorbs more strongly in the yellow and green than does the crystalline. By transmitted light its color is orange-yellow in films $\cdot 01^{\text{mm}}$ thick, and yellow in films $\cdot 001^{\text{mm}}$ thick.

The globules of which the pulverulent amorphous sulphide consists may have bright surfaces or surfaces dulled by wrinkles. In the former case the colors are most brilliant and pure. Powders consisting of separate globules $\cdot 0001$ to $\cdot 001^{\text{mm}}$ in diameter are bright yellow with a tinge of orange; powders having globules $\cdot 004$ to $\cdot 007^{\text{mm}}$ in diameter, or compact aggregates of smaller globules, are bright orange-colored. (See Table XII.)

The lumpy aggregates of dried flocculent precipitates have a duller orange color, owing to a less complete reflection of the light which enters the powder.

The characteristics of amorphous precipitates formed in various ways are given in Table XII, and the dispersion curve for the purest material at hand is shown in fig. 8.

A precipitate made by treating a 10 per cent solution of CdSO_4 + 20% H_2SO_4 with H_2S at boiling contained a few per cent of bright orange-yellow globules $\cdot 004$ to $\cdot 007^{\text{mm}}$ in diameter. These were cell-like, having a more highly refracting wall about $\cdot 001^{\text{mm}}$ thick.

Another precipitate made by heating for 2 days at 200° , 2 g. of amorphous CdS in a closed tube with 10 per cent HCl , was covered with a very thin film of indefinitely doubly refracting material having a much redder color than any other preparation examined.

Mercuric Sulphide.

Amorphous.—The tendency to aggregate into spherical masses, which is so marked in amorphous cadmium and zinc sulphides, has not appeared in amorphous mercuric sulphide.

Crystalline.—At least three crystalline modifications of HgS have been prepared. Of these, cinnabar crystallizes best, in sharply-bounded nearly equi-dimensional, red, hexagonal prisms

FIG. 8.

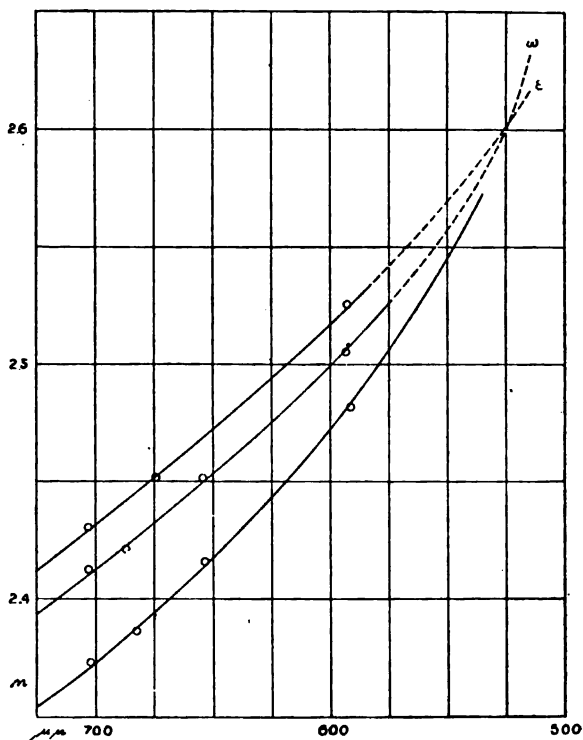


FIG. 8. Dispersion of greenockite and of amorphous cadmium sulphide.

or tables having very strong positive double refraction and very high refractive indices. The index ω of crystals formed by sublimation was approximately matched under the microscope in Li-light with a glassy mixture of Sb_2S_3 and As_2S_3 and found to be equal within the limits of error (about ± 0.02) to ω of natural cinnabar, i. e., 2.81; ϵ_{Li} , which is 3.14, is too high to be determined microscopically.

The new form, $\beta'\text{-HgS}$, is prismatic in habit and has not been produced in crystals exceeding 0.003mm in diameter and 0.03mm in length. These crystals always taper toward the ends

TABLE XII.

Method of preparation	Size of particles mm	Refractive index n_{Li}	Color	Remarks
Sodium thiosulphate in closed tube.....	·004 and less	2·38	Nearly pure orange	The purest orange examined Globules aggregated Clustered
Do	·001—·003	2·32	Orange	
H ₂ S cold.....	·0005	Orange-yellow	
H ₂ S and hot 5% HCl	·004	Orange	Aggregated
H ₂ S and hot 28% H ₂ SO ₄	·008	Deep orange	
Boiled several hours with sodium thio-sulphate.....	·007—·001	2·28 ±	Bright orange	
H ₂ S in the cold.....	·0005—·001	Yellow	
Na ₂ S, closed tube....	·001	2·40	Yellow	
Commercial powder heated dry at 500°	·0006	Yellow	
Commercial powder Sample 1.....	Compact aggregate	2·38—2·39	Dull orange	
Sample 2.....	Do	2·37	Do	

and have no distinct faces. They are commonly aggregated into stellate groups. In color they are not distinguishable from cinnabar, and like cinnabar are optically uniaxial and positive, but their refractive indices are lower and double refraction not so strong. ω of several lots of crystals was determined for wave-length about 650 $\mu\mu$. Monochromatic light could not be used advantageously on account of weak illumination and diffraction, but for the mean wave-length of the narrow band of the spectrum transmitted by the sulphur-selenium mixture in which the crystals were imbedded, the value of ω was found to be 2·60 to 2·61, the larger value being for the purest crystals. The dispersion of the crystals is not accurately known, but it appears to be about equal to that of the sulphur-selenium mixtures used. Therefore, for Li-light ω = about 2·58; $\epsilon\omega$ = 2·24 ± 0·03 according to several determinations on prisms of measured thickness.

The third modification, α' , is probably identical with the mineral metacinnabar, but positive identification is not possible on account of the minute size and poor development of the artificial crystals, and on account of the meager and conflict-

ing data on the crystallography of metacinnabarite. Crystals of this form are black, and when typically developed have six spindle-shaped rays, apparently equal and meeting at right angles. These characteristics indicate skeletal growth parallel to the axes of the cube. But numerous rays are present in some cases, and though the six can usually be distinguished, the exact relations of the intermediate rays are uncertain. None of the rays exceed $\cdot 01^{\text{mm}}$ in length.

In several preparations—previously described—black prisms were found which, in all but two cases, were shown to consist of transparent double salts coated with amorphous mercuric sulphide. In the two cases no satisfactory determination could be made.

Summary.

1. The two sulphides of zinc are enantiotropic: β -ZnS or sphalerite is stable below 1020° , where it is transformed into α -ZnS or wurtzite. Sphalerite has a density of 4.090, $\left(\frac{\text{mineral at } 25^{\circ}}{\text{water at } 4^{\circ}}\right)$. Wurtzite has a density very slightly less, viz., 4.087. The determinations were made on a very pure analyzed sphalerite, and the wurtzite formed by heating it to the proper temperature. The refractive indices of these forms for sodium light are: sphalerite, $n_s = 2.3688$; wurtzite, $\omega_s = 2.356$, $\epsilon = 2.378$.

2. Iron sulphide in solution lowers the inversion point of sphalerite strongly and in a nearly regular manner. The inversion temperatures of four analyzed ferruginous sphalerites, the highest containing 17 per cent of iron, were determined. The specific volumes of these sphalerites varied almost rectilinearly with the percentage of iron. The volume increases with the latter, although the specific volume of ferrous sulphide is only about 85 per cent as great as that of zinc sulphide. The refractive indices for sodium light of both sphalerite and wurtzite are raised 0.0033 for each per cent of ferrous sulphide.

3. Crystals of wurtzite of considerable size were obtained by sublimation at about 1200° – 1300° . Small dodecahedrons of sphalerite were obtained from molten sodium chloride at a little above 800° , while larger dodecahedrons as well as tetrahedrons crystallized from molten potassium polysulphide at about 350° . From aqueous solutions both sphalerite and wurtzite were obtained at temperatures between 200° and 400° . Below about 200° the products were amorphous. From solutions of alkali sulphides (alkaline solutions), *only sphalerite* formed; both dodecahedrons and tetrahedrons were obtained. From acid solutions of zinc salts hydrogen sulphide precipitates at 250° and above, both sphalerite and wurtzite. In nearly all cases (10 out of 12 experiments) so far as experiments have

gone, temperature and acid concentration have proved the definitive factors. The higher the temperature for a given acid concentration the greater is the percentage of sphalerite (the stable form) crystallized; and the higher the acid concentration for a given temperature the greater is the percentage of wurtzite (the unstable form) crystallized.

Quantitative work has shown previously that the same rule holds for the disulphide of iron. Here the *stable* form is *pyrite* and the *unstable*, *marcasite*.

4. A preliminary study was made of the precipitation of zinc by hydrogen sulphide from solutions of variable acid concentration.

5. We have obtained only one sulphide of cadmium, the mineral greenockite, whatever method was used in its preparation. Very pure large crystals were prepared by Lorenz' method, viz., the action of hydrogen sulphide on cadmium vapor. The density of these crystals, $\frac{\text{mineral at } 25^\circ}{\text{water at } 4^\circ} = 4.320$.

The refractive indices were found to be $\epsilon_{Na} = 2.529$, $\omega_{Na} = 2.506$.

The various hues of different preparations of cadmium sulphide do not depend, as has been claimed, upon different allotropic forms; they depend first on whether the substance is crystalline or amorphous. The color of the amorphous products depends chiefly on the size of the grains, the yellow products consisting of more minute particles, but it is also influenced by the nature of the surface of the individual grains, and their forms.

6. Mercuric sulphide exists in three different crystalline forms, viz.: cinnabar, $\alpha\text{-HgS}$, which is readily prepared by digesting any other form of mercuric sulphide with a solution of ammonium sulphide or alkali sulphide; metacinnabar, $\alpha'\text{-HgS}$, which is precipitated from *dilute* acid solutions of mercuric salts by sodium thiosulphate; and a new crystal form, $\beta'\text{-HgS}$, which is obtained from *more concentrated* neutral solutions of mercuric salts in a similar way.

The density of cinnabar, $\frac{\text{mineral at } 25^\circ}{\text{water at } 4^\circ} = 8.176$.

The specific gravity of $\alpha'\text{-HgS}$ at 25° averaged 7.60 as compared to about 7.7 for the natural mineral. For reasons stated in the text the latter figure is doubtless too high.

$\beta'\text{-HgS}$ has only been obtained in the form of a fine crystalline powder, having practically the same color as vermilion. It is hexagonal. The specific gravity at 25° averaged 7.20. The indices of refraction for $650 \mu\mu$ were: $\omega_{Li} = 2.61$, $\epsilon_{Li} = 2.85$.

7. Cinnabar is the stable form of mercuric sulphide at all temperatures up to its sublimation point, which is about 580° .

The other two forms change into it, either by heating alone or more readily in the presence of solvents like concentrated ammonium sulphide or 30 per cent sulphuric acid. The absorption of light by cinnabar increases markedly with rising temperature, but it regains its color on cooling after long heating at 325°. Heated above 400° it becomes permanently black. This is not an inversion as some have supposed; the cinnabar contains only about 1 per cent or less of a thin coating of the black sulphide which perhaps is caused by condensation of the vapor.

8. Amorphous cadmium sulphide is so fluid, that during precipitation small particles may aggregate into globules 0.005 to 0.01^{mm} in diameter which remain permanently plastic. Amorphous zinc sulphide aggregates similarly but the globules may harden, either without crystallizing, or by crystallizing. In the former case they simulate doubly refracting spherulites owing to the development of strains in a wholly amorphous substance; in the latter case double refraction is due to wurtzite.

9. Comparing the genetic relations of the minerals sphalerite, wurtzite, cinnabar and metacinnabar with the genetic relations of pyrite and marcasite, we find certain remarkable regularities. The *stable forms*, sphalerite, cinnabar and pyrite are always obtained by crystallization from alkaline solutions (solutions of the alkali sulphides), while the *unstable forms* wurtzite, metacinnabar and marcasite are obtained from acid solutions only. The stable forms also may be crystallized from acid under certain conditions. Of these temperature and acid concentration appear to be the important ones.

Certainly with pyrite and marcasite and in all probability with sphalerite and wurtzite, the higher the temperature the greater is the percentage of the stable form obtained, while the higher the acid concentration at any temperature the greater is the percentage of the unstable form obtained. These facts appear to agree remarkably well with the field evidence which relates to the genesis of the natural minerals, while they give new significance to the general geologic distinction between deep-seated and surface waters in nature.

10. None of the sulphides of the group zinc, cadmium, mercury melts at atmospheric pressure.

In conclusion the authors wish to express their thanks to Dr. Geo. P. Merrill of the National Museum for placing at their disposal much valuable material for study; to Mr. C. E. Siebenthal of the U. S. Geological Survey for mineral specimens, and to Mr. B. S. Butler, and especially to Mr. Waldemar Lindgren, also of the U. S. Geological Survey, for geological data and valuable criticism.

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D. C., July 9, 1912.

SCIENTIFIC INTELLIGENCE.

I. CHEMISTRY AND PHYSICS.

1. *The Formation of Red Phosphorus*.—The usual, well known, method of converting colorless phosphorus into the red modification consists in heating the substance in closed vessels for some time at about 250°C ., a temperature near its boiling-point. STOCK, SCHRADER and STAMM have now found that when the vapor of phosphorus is highly superheated and then quickly condensed, a considerable amount of red phosphorus is found in the product. Experiments were made by heating the vapor in tubes of quartz glass to various temperatures and suddenly cooling by plunging the hot tubes into cold water. In this way it was found that after heating to 450°C . the condensed product was slightly colored, and that the amount of red phosphorus formed increased, as the temperature of heating was higher, up to 1175°C . and above. The duration of the heating was found to have little effect, but the rapidity of the cooling was of the greatest importance. For instance, when a tube heated to 700°C . was immediately cooled the product was very red, if the cooling was delayed two seconds after removing the tube from the furnace there was very little red phosphorus produced, after a delay of five seconds there was only a trace, and when the tube was allowed to cool in the air the condensed phosphorus was almost colorless. Under favorable conditions of high heating and very rapid cooling it was found that as much as about one-third of the total phosphorus was obtained in the red modification. It has been known for a long time that the vapor of phosphorus has a density at $300\text{--}400^{\circ}\text{C}$. corresponding to the molecular formula P_4 , while at higher temperatures the molecule becomes smaller, being intermediate between P_4 and P_2 at 1700°C . It is the opinion of the authors that the sudden cooling of the superheated vapor causes the molecules that are smaller than P_4 to combine either with the latter or with each other to form red phosphorus molecules. They do not believe that the molecule of red phosphorus is smaller than that of the colorless substance, since all the properties of red phosphorus indicate that the opposite is true.—*Berichte*, xlv, 1514. H. L. W.

2. *Devitrification of Silica Glass*.—The use of apparatus blown and worked from melted quartz has become very common in chemical laboratories, on account of the resistance of the material to solvents, its high melting point, and its remarkable endurance of sudden changes in temperature. Several years ago it was found that silica glass is permeable to helium and to hydrogen at a low red heat, and now Sir WILLIAM CROOKES has observed that the material when kept for a long time at a high temperature becomes devitrified and opaque, and then permits

the passage of air through the walls of an exhausted vessel. He found that a perfectly transparent bulb of quartz glass when kept at 1300° for twenty hours in an electric resistance furnace became white and translucent like frosted glass, and with several exhausted bulbs treated similarly he found a very considerable leakage of air. The leakage was found to occur not only while a bulb was heated but also at ordinary temperature after devitrification had taken place. A micro-photograph of a devitrified silica bulb showed a surface cracked all over into the appearance of cells, and many of the cells showed a decided hexagonal outline. Crookes has observed a similar appearance when a silica dish, originally clear and transparent, was used for evaporating the solution of 100msr of pure radium bromide. Patches appeared on the bottom having a dull, roughened appearance, and upon microscopic examination they showed a structure very similar to that of the devitrified bulb. He concludes that radium at the temperature of boiling water can devitrify quartz glass, but he has not seen this effect upon the surface of glass or silica bottles in which radium salts have been kept in the cold for several years. — *Chem. News*, cv, 205.

H. L. W.

3. *The Presence of Formaldehyde in Plants.*—According to Baeyer's assimilation hypothesis, the plant first reduces carbonic acid to formaldehyde, and then condenses this to carbohydrates. In order to establish this hypothesis it is of great importance to detect the presence of formaldehyde in plants. CURTIUS and FRANZEN show that all the tests that have been previously used for this purpose have been unreliable on account of the interference of other aldehydes, and they conclude that formaldehyde in plants has not been detected heretofore. Therefore, these chemists have made a new investigation of the subject, and it appears that they have definitely established the presence of formaldehyde in the leaves of a certain plant, and have thus established the basis of Baeyer's theory. They used the leaves of a certain kind of beech, "Hainbuchenblätter," in large quantity. As much as $1\frac{1}{2}$ tons of the leaves, altogether, were put through the process, which was an elaborate one consisting of several distillations, the conversion of the aldehydes into the corresponding acids by means of silver oxide, and after further separations the final detection by several methods of the resulting formic acid. Quantitative determinations showed that 1g of the leaves contained only 0.00086g of formaldehyde, or less than one part per million. — *Berichte*, xlv, 1715.

H. L. W.

4. *The Determination of Sulphur in Insoluble Sulphides.*—T. ST. WARUNIS, having previously worked out a method for the determination of sulphur in coals, has applied the same principle successfully to the analysis of sulphides. A portion of 0.5g of the sulphide, ground exceedingly fine, is intimately mixed in a spacious porcelain crucible with a mixture of 4 parts of dry sodium carbonate and 3 parts of copper oxide, the whole is covered with a thin layer of the same mixture and is heated gently

at first, then finally for 2 hours at the full heat of a Bunsen burner. During the heating the mass must be frequently stirred with a strong platinum wire, and it is advisable to place the crucible in a hole in an inclined piece of asbestos board during the ignition, in order to protect its contents from the sulphur of the flame. After cooling, the mass is extracted with water, the solution is filtered, the residue is boiled with sodium carbonate solution and finally washed with water. The solution is acidified with hydrochloric acid, evaporated to dryness to separate silica, and the sulphur finally determined as barium sulphate in the usual manner. The author states that in this way he has obtained very good results more conveniently and quickly than by the usual methods, and he gives test analyses upon copper pyrites, iron pyrites, and mercuric sulphide which show very satisfactory results.—*Berichte*, xlv, 869. H. L. W.

5. *Benzoic Acid as an Acidimetric Standard*.—Although the employment of organic acids for this purpose is not new, it is interesting to notice that G. W. MOREY has used benzoic acid with very satisfactory results. It was found best to fuse the bulky sublimed acid before weighing by heating it in a platinum dish to about 140° C. The fused material can then be broken up and kept indefinitely for use. Phenol phthalein was used as the indicator with the careful exclusion of carbonic acid. The material has the advantage of high molecular weight, so that comparatively large quantities can be used, thus reducing the errors in weighing. It is also easily obtained in a pure condition, it is stable and not hygroscopic.—*Chem. News*, cvi, 66. H. L. W.

6. *Ein neuer Fall von Koppelung kurz- und langwelliger Fluoreszenzbanden*.—According to Stark's theory of band spectra two kinds of absorption bands are to be distinguished. The criterion for differentiation depends on the behavior of the bands when the attempt is made to stimulate fluorescence. The so-called long-wave bands have the property of absorbing light without appreciable fluorescence. On the other hand, absorption of light by a "short-wave" band is, in general, accompanied by the emission of fluorescent light not only in its own interval of wave-lengths but also in the region of the "coupled" long-wave band. Furthermore, the absorption is more intense for the short-wave bands than for the associated long-wave bands.

It has been shown by Stenbing that mercury vapor affords a practical example of coupled absorption bands. The discovery of three other concrete cases by M. GELBKE is obviously a matter of theoretical importance. The substances which he has shown to possess coupled absorption bands are acetone (CH_3COCH_3), diacetyl ($\text{CH}_3\text{COCOCH}_3$), and ethylcyanid-monoxal-ethylester ($\text{N}_2\text{H}_5\text{C}_2\text{COCO}_2\text{C}_2\text{H}_5$). These ketones were dissolved in very pure ethyl alcohol.

The source of light employed was a strong spark between electrodes made of an alloy of iron and tungsten. The condensing lens was of quartz and the spectrograph had fluorite objectives

and a single 60° prism of the last named material. The absorption cell and the general assemblage of apparatus were set up in the usual manner. As already implied, the positions and intensities of the bands were recorded photographically.

The maxima of the absorption bands of acetone are shown by the curves to have the approximate wave-lengths $275\ \mu\mu$ and $355\ \mu\mu$ respectively. The fluorescence bands extend from $260\ \mu\mu$ to $320\ \mu\mu$ and from $325\ \mu\mu$ to $460\ \mu\mu$. The former has a minimum of emission at $300\ \mu\mu$ and the latter at $340\ \mu\mu$. In other words, each fluorescent band seems to be double. For the concentration used, "1:320", the greatest intensity of fluorescence falls at $360\ \mu\mu$. For diacetyl the maxima of absorption lie at $285\ \mu\mu$ and $410\ \mu\mu$. The shorter wave-length fluorescent band is also double and comprises the interval $270\ \mu\mu$ to $350\ \mu\mu$, the minimum being shown graphically at $320\ \mu\mu$. The longer wave-length fluorescent band is single and extends from about $355\ \mu\mu$ to $480\ \mu\mu$. The fluorescent maximum comes at $410\ \mu\mu$ for a concentration of 1:620. For ethylcyanid-monoxal-ethylester the maxima of absorption have the wave-lengths $335\ \mu\mu$ and about $430\ \mu\mu$. Both fluorescent bands are single, the one extending from $290\ \mu\mu$ to $365\ \mu\mu$, and the other from $395\ \mu\mu$ to below $480\ \mu\mu$. For the concentration employed, 1:11200, the intensity of emission is greatest at $435\ \mu\mu$.

The three ketones satisfy the requirements for "coupled" bands. That is, when the wave-lengths of the exciting light lie within the more refrangible absorption bands, both fluorescent bands come out strongly, provided, of course, the concentration is appropriate for observation. On the other hand, fluorescence is not appreciably produced when the wave-lengths absorbed are confined to the region of the less refrangible absorption bands. Although the absorption is much greater in the short-wave than in the long-wave bands, nevertheless the more refrangible fluorescence is markedly less intense than the less refrangible fluorescence. This is doubtless due to the excessive absorption of the shorter wave-length fluorescent light by even thin layers of the solution. According to Stark's theory, the "centers" of the absorption and fluorescent bands of the substances under consideration are the valence electrons of oxygen which are loosely bound to carbon.—*Physikal. Ztschr.*, No. 13, July, 1912, p. 584. H. S. U.

7. *Die Ionisierung von Gasen durch Licht und das Funkenspektrum des Aluminiums im Gebiete der Schumannstrahlen.*—Certain spectrograms taken by THEODORE LYMAN have enabled him to bring out some interesting and important facts relating to the spectra of the sources of light used by Lenard and others in the study of the ionization of gases by ultra-violet light. The region under consideration extends from wave-length $1200\ \text{\AA. U.}$ to about $1870\ \text{\AA. U.}$ The first positive reproduced shows the spectrum of a spark between aluminium electrodes in an atmosphere of hydrogen. A comparatively small number of lines

(about 20), and no continuous background can be seen on the plate. The shortest wave-length recorded photographically is about 1370 Å. U. The second spectrogram was obtained when the aluminium electrodes were placed so close to the fluorite window of the vacuum grating-spectrograph as to cause the discharge to play along the surface of the window. The exposure lasted six minutes and the fluorite was badly damaged. However, notwithstanding the latter incident, the spectrogram is very good, the lines are much stronger than in the positive first mentioned, additional lines appear in the neighborhood of λ 1300, and a dense, continuous background fills the region from λ 1650 to λ 1870. In fact, most of the energy seems to be concentrated in the last named interval. (The plates do not extend to wave-lengths greater than 1870 Å. U.) The electrical apparatus used by Lenard was more powerful than that employed by Lyman.

From another point of view, Lyman has shown in earlier papers that a quartz plate, one or two millimeters thick, is quite transparent below 1600, but that it is "absolutely" opaque for wave-lengths shorter than 1400. Furthermore, he has demonstrated experimentally that air is very opaque between 1400 and 1550, but that transparency begins again at about 1350.

When all of the facts just enumerated are taken into account the conclusion must be reached that the "rays" with which Lenard was dealing consisted in the strong aluminium group at about λ 1300. For, Lenard says:* "Die auf Luft wirksamen Strahlen werden also zum weitaus grössten Teile durch Quarz absorbiert, und zwar ausserordentlich viel stärker durch den Quarz als durch die gleich dicke Luftschicht, welche er ersetzte."

The third and last spectrogram illustrating Lyman's paper pertains to the vacuum-tube spectrum of hydrogen. In obtaining this plate no capacity was introduced in the secondary circuit, a current of about 10 milliamperes flowed, and the gas was at a pressure of about 2 millimeters of mercury. The spectrum consists of so many fine lines as to give a nearly continuous, strong and uniform illumination from about λ 1330 to λ 1640. In the same interval the spark between aluminium electrodes gives only a few scattered lines. Also the hydrogen spectrum has a group of fine lines between λ 1230 and λ 1290. Consequently, Lyman recommends the hydrogen vacuum-tube for use in experiments on ionization. The fact that Palmer, working with a vacuum-tube, obtained nearly as great volume ionization as Lenard, although the latter had a very powerful transformer, is also accounted for by the foregoing data.—*Physikal. Ztschr.*, No. 13, July, 1912, p. 583.

H. S. U.

8. *On the Apparent Change in Weight during Chemical Reaction.*—This question has been recently investigated by J. J. MANLEY. Although he gives only an abstract of the original paper, nevertheless the salient points and the final result seem to be of sufficient general interest to merit attention in this place. Manley first points out that Landolt, in his classical investigations, seems to have omitted taking precautions against certain

* Sitzungsber. d. Heidelb. Akad. d. Wiss., Abth. 24, 1911, p. 19.

possible sources of error, doubtless deeming them of negligible importance. These errors may arise from (1) air streams within the balance case, and (2) differences in the superficial areas of the reaction vessels and the consequent possibility of a variation in the relative masses of any aqueous films which may be formed on the surfaces. Furthermore, evidence is lacking in Landolt's memoir to show that he paid sufficiently close attention to effects producible by very slight and varying differences in the temperature of the contents of any pair of his reaction vessels. Since Manley considered these sources of error as extremely important he accordingly introduced devices for eliminating and neutralizing the errors just indicated.

A new and hitherto unsuspected secondary chemical reaction occurring within the reaction vessels was discovered and partially investigated. This reaction may be somewhat accelerated by heat and greatly so by the radiations from a tantalum lamp. It was shown that this phenomenon made it impossible to obtain trustworthy results with solutions of silver nitrate and ferrous sulphate. Decisive results could be obtained with solutions of barium chloride and sodium sulphate because these salts react quickly and practically perfectly.

The limit of accuracy estimated by Landolt, under his working conditions, was ± 0.03 mgrm., while Manley claims ± 0.006 mgrm., just five-fold better. Landolt found the mean apparent change in mass during chemical reaction to be not greater than 1 in 1×10^7 . In the most thoroughly investigated case, in which the reacting bodies were barium chloride and sodium sulphate, Manley found that the apparent change in mass did not exceed 1 in 1×10^9 .—*Proc. Roy. Soc.*, vol. lxxxvii, No. A 594, p. 202.

H. S. U.

9. *On the Torque produced by a Beam of Light in Oblique Refraction through a Glass Plate.*—In the presidential address to the Physical Society in 1905 Poynting developed the idea that a beam of light must be regarded as containing a stream of momentum, and he showed that this principle may be used to solve with great ease the various cases in which a beam of light is absorbed, reflected, or refracted at a surface. The particular case in which a beam of light is refracted at a plane surface was also analyzed by Poynting and the conclusion was drawn that there will always be an outward pull along the normal, *i. e.* from the more dense towards the less dense medium. Hence, when a beam of light passes obliquely through a parallel plate there is a normal pull outwards both at incidence and at emergence, and these two pulls constitute a couple. Obviously, the forces arising from the several reflections in any actual piece of apparatus must be taken into account in making numerical calculations. Preliminary quantitative experiments were performed by Poynting and Barlow with the object of comparing the observed torque with the value of the couple derived from the principle of luminiferous momentum. However, the apparatus used did not yield very satisfactory results.

Since that time G. BARLOW has devised and used an apparatus

which is largely free from the sources of error which vitiated the earlier work. The new system consists essentially of a cube of crown glass suitably suspended by a brass rod and a quartz fiber. The cube was made as perfect as possible and, when suspended, four of its edges were vertical and parallel to the axis of rotation. The horizontal beam of light passed diagonally through the cube and experienced two refractions and only two primary reflections. The suspended system was enclosed in a gun-metal box which was fitted with the necessary lateral tubes, windows, etc.

Details of the precautions taken with respect to "gas action" and convection currents may be omitted in this place. Also, the calculations of the torque, of the reflection corrections, and of the energy density of the beam of light afford no novelty. It is worthy of note, however, that Barlow found hydrogen far more reliable than air inside of the box enclosing the suspended system. The calculated and observed deflections agree as well as can be expected when the inherent difficulties of the experiments are given due consideration. The observed deflections are systematically larger than the calculated deflections, which shows either that some source of error has been overlooked or that a fundamental datum was not determined with sufficient accuracy. Nevertheless the following statement of the author seems justified by the final results, namely: "We may therefore conclude that the oblique passage of a beam of light through a plate of refracting material produces on the matter of the plate a torque which has the magnitude deduced from the transfer of momentum in the beam."—*Proc. Roy. Soc.*, vol. lxxxvii, No. A 592, p. 1.

H. S. U.

II. GEOLOGY.

1. *Sub-Oceanic Physiography of the North Atlantic Ocean*; by Prof. EDWARD HULL. Atlas with eleven folio maps in color. London (Edward Stanford).—The maps here given show in better form than anything previously published, the borders of the continental platforms, indented by valleys and embayments, and further crossed by great river-like valleys and canyons, extending from the present continental rivers, such as the Hudson channel, as first noticed by Professor J. D. Dana; and later built up into systems by Spencer, Hull, and Nansen, in order of time. Hull's charts show the indented borders of the Eastern Continents, like those of high plateau regions, and also many submerged river-valleys, such as those of the English Channel River, Irish Sea River, the canyons of the Adour and Tagus, of the Congo, and others in the Mediterranean; while in a condensed form, the numerous submarine valley-systems off the American coast, as developed by the reviewer, are added, thus making the subject more complete. Hull is led to conclude that these high plateaus were the courses of former land valleys, and accordingly in them are found means of measuring the late changes of land and sea. The former high elevations and continental extensions are supported by the distribution of animals and plants, and late glacial

conditions. Conversely, the epoch is regarded as primarily due to elevations, now measurable, with the consequent deflection of the Gulf Stream. Even where some are indisposed to accept this conclusion as to the cause of the Glacial Period, no other explanation of the origin of these submarine channels has been shown to obtain, which interpretation has been given to them in this country by Dana, Chester, Lindenkohl, Davidson, Branner, Upham, and the reviewer, all who have investigated the problems at first hand.

The data, shown in graphic form, are indispensable, both the physiographic as well as the oceanographic, and the whole constitutes a worthy monument of the labors of the author, which must be lasting so long as interest in the Earth's studies lasts. These studies had been almost passed over by the earlier oceanographic writers, but they are so widespread that their study constitutes a new brand of science, which Hull most generously attributes to the reviewer as the founder, by his work on the Antillean region and off the American Coast. J. W. S.

OBITUARY.

JAMES TERRY GARDINER, the civil engineer, died at North East Harbor, Maine, on September 10 in his seventy-first year. He was born at Troy, N. Y., on May 6, 1842, and was educated at the Rensselaer Polytechnic Institute and at the Sheffield Scientific School; receiving the honorary degree of Ph.B. from the latter institution in 1868. His labors as an engineer were carried on in connection with the Brooklyn water works, with the construction of earthworks around the harbor of San Francisco, and elsewhere. His most important work was as a topographer, first with the Geological Survey of California, 1864-67; later with the Survey of the 40th Parallel under Clarence King, 1867-72; and also the U. S. Geological Survey under F. H. Hayden, 1872-75.

DR. WILLIAM J. MCGEE, the geologist and anthropologist, died at Washington on September 4 at the age of fifty-nine years; a notice is deferred till a later number.

DR. PAUL CASPAR FREER, for ten years the able director of the Bureau of Science in the Philippine Islands, died at Baguio on April 18 in his fifty-first year.

HENRY ADAM WEBER, professor of agricultural chemistry at the Ohio State University, died on June 14 at the age of sixty-seven years.

JULES HENRI POINCARÉ, the distinguished French mathematician, died on July 17 at the age of fifty-eight years.

PROFESSOR CHARLES ANDRÉ, the French astronomer and director of the Lyons Observatory, died on June 6 at the age of seventy years.

DR. HUMPHREY OWEN JONES, the English chemist, lost his life in an Alpine accident on August 15 in his thirty-sixth year.

DR. RUDOLF HÖRNES, professor of geology at Gratz, died on August 20 at the age of sixty-two years.

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[FOURTH SERIES.]

ART. XXXVI.—*Volcanic Vortex Rings and the direct conversion of Lava into Ash*; by FRANK A. PERRET, K.I.C.
Volcanologist of the Volcanic Research Society.

THE vortex rings projected from cannon, locomotives, the mouth of a smoker, etc., are familiar to all. Sudden puffs from any smoke-filled cavity will produce, by interference at the edges of the orifice, visible annular vortices having a certain stability of form due to the persistence of the vortical movement. It is obvious, therefore, that the conditions necessary for the production of these rings must often obtain at volcanic craters and, in fact, such volcanoes as Vesuvius and Stromboli, during the prolonged periods of moderate activity which may be said to constitute their normal condition, project large, thin rings of vapor which frequently attain diameters of five hundred meters or more. Generally speaking, these are somewhat difficult to photograph because of their delicacy and lack of photographic contrast with the sky, and it was not until the Etna eruption of 1910 that the present writer observed volcanic vortex rings having a sufficient degree of solidity to permit of satisfactory photography. Figs. 1 and 2 show the type of rings projected at that time and of which the diameters were approximately 150 and 200 meters. It is not, however, with the purpose of discussing vortex rings, as such, that I have here referred to this phenomenon but because of the fact that these particular rings of the Etna eruption illustrate a principle of volcanic action which is of such importance as to merit attention at this time.

What impressed me most in observing these rings was the fact that they were composed almost entirely of *ash* and yet had been projected from a crater yielding *liquid lava*. This was the lowermost of the seven principal groups into which the twenty or more vents of this eruption were con-

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formed and, according to my own enumeration, which has been generally adopted, viz. from the upper end of the fissure downward, it is known as crater No. 7.

The outflow of lava, which at the beginning had taken place at many points along the line of the fissure, was soon localized, as is normally the case, at the lowest principal opening, and this continued to be the source of the magnificent stream which formed so spectacular a feature of this eruption. (Fig. 3.)

The gas content of the magma caused a semi-explosive emission, projecting sprays and jets of incandescent liquid masses

FIG. 1.



to a considerable height (fig. 4), the result of which was the gradual building up of a cone of the compacted scoriæ, best seen in the post-eruption view (fig. 5). It is important to note that neither the ejected fragments, nor the walls of the crater, nor the upper portion of the cone were "dry," i. e., hard or brittle, and therefore capable of being broken or crushed to powder—all were in the liquid or viscous state. There was no demolition of the cone itself, which was growing by accretion, and there was present no old material whatever, yet this crater constantly emitted a quantity of ash-laden vapor having a salmon-pink tint.

On the 30th of March at 6 A. M., the writer was proceeding along the line of eruptive mouths, when the rings shown in

figs. 1 and 2 were projected from crater No. 7. These had the same color as the other vapors and the air was full of a fine red ash having a strongly acid reaction. The large amount of this ash present in the air may be inferred from the aspect of the sun in the lower portion of fig. 2, which appeared as a ball of burnished copper, and was photographed without irradiation effects.

This production of ash continued along the first few hundred meters of the lava stream where the gases still escaped from the surface in considerable quantities. The gas emission under these

FIG. 2.



conditions is apparently very gentle (fig. 6), producing a continuous simmering sound analogous to that of water in a kettle just before ebullition, but it is probable that each tiny gas vesicle burst from the lava with an explosion *which, for its size, is violent*, and thus projects and carries off minute particles of the exploded shell.

It is this *subdivisional* gaseous expansion, and not the explosion of large bubbles, which is the cause of the formation of the ash.

The degree of viscosity of the lava is, in all probability, an important factor in this direct formation of ash, while secondary to the gas content as a determining cause. In the case we are considering, although the velocity of the stream at this locality

was five meters per second and the mass as a whole showed all the qualities of a liquid, the viscosity was so great, especially in the outer layer, that a heavy rock thrown upon the surface rebounded as from a plate of steel, and it was only with the greatest difficulty that an iron rod could be forced into the moving stream. In the very liquid lavas of Hawaii the gas vesicles issue almost without resistance and do not form ash in this way, but large gas bubbles scatter the lava and spin it out into glassy filaments—the well known “Pele’s Hair.”

The present writer has often observed the same copper-colored cloud of gas and ash as produced directly from glowing lava in the central crater of Etna, and also in that of Vesuvius

FIG. 3.

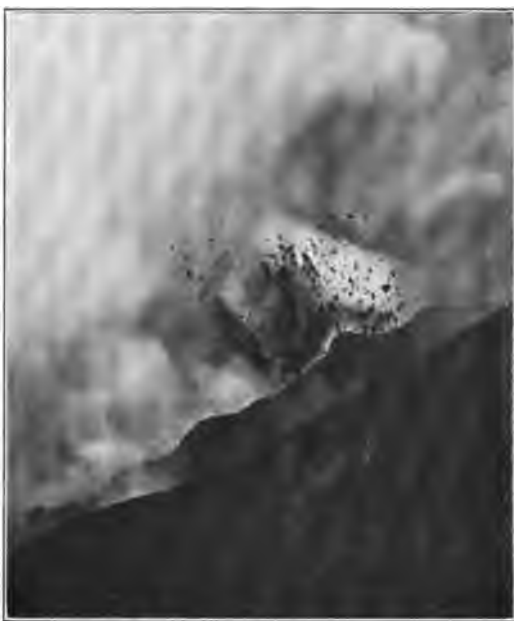


and Stromboli. A cloud of *white* vapor over the crater will also, even in daylight, under these circumstances, appear of a copper tint because illuminated by the glare of the lava below, but when ash is present the color of the cloud persists to all distances, as in the case of the Etna rings.

Let us now leave the consideration of the principle as exemplified in this superficial action, and study its function in the more fundamental processes of a great eruption. Taking the Vesuvian outbreaks of 1872 and 1906 as typical, and glancing at conditions at the outset, we find that as the result of a long period of moderate activity the cone has been built up to a considerable elevation above the crater of the preceding great eruption, and that the lava stands at a commensurately high

level in the central conduit. At the initiation of the eruption the cone is fissured laterally by pressure, fusion and gas tension causing a rapid and copious outflow of lava. This is accompanied by a more or less complete demolition of the upper portion of the cone, the explosive effects at the central vent increase in violence, ejecting old and new material, and attain their maximum with the cessation of the lava outflow, to which there succeeds the truly stupendous emission of gas and ash from the main crater (fig. 7)—no more liquid lava being seen.

FIG. 4.



But if, in such a case, we are asked to consider the liquid outflow and the explosive ejections as constituting the only emission of co-eval lava, and the ash as being merely old cone-material and triturated rock, as is quite generally supposed, then, I believe, I may raise a point of objection and interrogation.

Let us consider for a moment the condition of the magma in the deeper portions of the volcanic conduit. Its temperature will be higher and its gas tension greater than in the upper portion while it will be subjected to the pressure of the column above it. In these respects it is analogous, as I pointed out

some years ago,* to the water in the lower portions of a geyser or to the water in a boiler under tension. This, by reason of the pressure upon it, is actually in liquid form, but it is potentially a vapor because of its temperature, and if the pressure is removed it will flash into the gaseous condition. Similarly, the lower zones of lava in the volcanic conduit are potentially in a condition of explosive extension and are maintained in a liquid or semi-liquid state only by the pressure from above. If now we imagine a relief of this pressure—say by a lateral outflow of lava sufficiently rapid and copious to materially

FIG. 5.



reduce the height of the lava column—a powerful gaseous expansion will be initiated in the magma below and this will extend progressively downward with progressive relief of pressure from above. This gaseous development will be *distributed, subdivisional, intermolecular*, the magmatic mass expanding to a froth and being finally ejected as a cloud of gas and ash—it is impossible that it should appear in a liquid form under these conditions.

Note that this ash will have been formed under very different conditions from that which is blown off from the surface of the lava in the crater during the early part of the eruption. This latter is formed in contact with atmospheric air and is quickly cooled; it is, therefore, of a vitreous nature with surface oxidation. But the ash from the depths will have

* "Some Conditions affecting Volcanic Eruptions." *Science*, Aug. 28, 1908.

been formed in a bath of the magmatic gases, out of contact with the atmosphere, and at a temperature which is maintained for a considerable time. The difference between the two is, however, mainly physical, and the magmatic ash, if I may so call it, should also, by the very conditions of its formation, be *virtually identical*, as material, with the co-eval lava, i. e., its ingredients should be the same, it should carry the same salts, exhibit the same crystals under the microscope, give off the same gases on being heated, etc., which could hardly be the case if it were formed by the trituration of old and profoundly

FIG. 6.



metamorphosed rock. The limits of the present paper will not permit of a full discussion of this important subject, but it may be noted that Palmieri,* writing of the Vesuvian ash of 1871 and 1872, refers to its identity of composition with the co-eval lavas, and Casoria's analyses of the 1906 products show this to a remarkable degree; it is evident that some of the old trituated material must be found in the ash, the present contention being that it does not constitute the bulk of it.

Considering this in connection with the fact that those who have attempted to calculate the total volume of material lost by the cone have generally considered it insufficient to account for the amount of ash emitted, we may fairly state the necessity of admitting the emission of co-eval magmatic material during the ash phase of the eruption.

* "The Eruption of Vesuvius in 1872." L. Palmieri (page 119.)

It will be seen that this hypothesis does not in the least degree invalidate the division of the eruption into a "Strombolian" and a "Vulcanian" phase—on the contrary, it supplies a cause for the great and continued dynamism of the "Vulcanian" phase and explains the identity of its ash with the co-eval lava.

FIG. 7.



It is interesting to note that the "Vulcanian" phase, as far as actual, external eruption is concerned, is cooler than the "Strombolian." This is due, in part, to the downward removal of the furnace, i. e., the lava column, but also, most certainly to the enormous absorption of heat in the process of gaseous expansion in the deeper magma and the subdivision of the latter into minute particles which quickly assume the temperature of the gas which surrounds them. During the "Strombolian" phase

the incandescent lava in the crater is thrown into the air in large masses by great gas bubbles rising through the liquid, without material alteration of its temperature, but the magma of the depths, if our theory be true, is atomized, so to speak, into a gaseous emulsion whose temperature, although initially above that of the crater lava in the "Strombolian" phase, will be very quickly lowered by the enormous expansion—a degree of extension which can only be fully appreciated by one who, like the present writer, witnessed at close range the great emission of April 8th, 1906, whose volutes of vapor, even at the height of two kilometers, still expanded with an incredible acceleration in all directions. No witness of that great, continuing, trepanning blast could ever be persuaded that there remained in the throat of the volcano any broken solid materials whose trituration should furnish the ash of that and the following days, according to the ordinary conception.

We must accept the absorption of heat by gaseous expansion as the cause of a lower temperature or else admit for the depths of the volcanic conduit and the magmatic pocket or fissure a temperature inferior to that of some intermediate zone, as is often the case with geysers. The "Vulcanian" phase needs study.

Considering this principle of direct ash production as it may obtain in the phenomena of volcanoes of different types, it would seem that the highly viscous lavas of andesitic and trachytic nature might explode subaërially, upon sudden relief of pressure, into gas and divided solid material, causing such effects as the "Nuées Ardentes" of Mt. Pelée. At the other extreme, the ultrabasic Kilauea shows ash strata several meters in depth and ash fields many kilometers in extent, and there seems no reason to doubt that a sufficiently rapid outflow at a low level will cause even the Hawaiian subjacent lavas to froth up and be ejected as ash.

In this connection it may be noted that Dana,* writing of the thread-lace scorix of Kilauea, suggests that a further subdivision or frothing of the material might produce ash, and claimed for such a process an explanation of ash formation more reasonable than the trituration of rocks. Taking this with the many comments on the identity of ash and co-eval lava, it would seem that only a dynamic theory was required for the rounding out of a complete hypothesis. May not this conception of a subdivisive, intermolecular gaseous development and expansion in subjacent magma, upon relief of pressure from above, be accepted as a plausible explanation of the observed facts?

Naples, July, 1912.

* "Characteristics of Volcanoes." (Page 166.)

ART. XXXVII.—*On Quartz from Alexander County, North Carolina*,* by J. E. POGUE in Washington and V. GOLDSCHMIDT in Heidelberg.

THE complex development of quartz crystals from Alexander County has been set forth in an important and thorough contribution by G. vom Rath.† This occurrence, however, shows such a wealth of forms that further investigation yields many new ones.

In the United States National Museum at Washington there is a large number of crystals from this source, and the private collection of V. Goldschmidt at Heidelberg also includes an extensive series. Two crystals of peculiar interest, chosen from the two collections, form the subject of this paper. Their description may serve at the same time as an illustration of the methods employed in an investigation of this kind. The measurements were made upon the two-circle goniometer in Heidelberg.

CRYSTAL 1. (U. S. National Museum. Cat. No. 82917.) Dimensions: $9 \times 15^{\text{mm}}$. *Right-handed*. Figs. 1a, 1b, 1c, show the crystal from three sides in natural development. The distribution of the faces is represented in the gnomonic projection (fig. 3). The forms identified appear in the following table:

Letter	<i>b</i>	<i>r</i>	<i>ρ</i>	ϕ *	<i>h</i>	κ	<i>g</i>	θ	<i>f</i>	δ
Symb. Gt. <i>pg</i> ..	$\infty 0$	+10	-10	$-\frac{1}{2}0$	+20	-20	+30	-30	+40	-60
— Bravais .	10 $\bar{1}0$	10 $\bar{1}1$	10 $\bar{1}1$	9097	20 $\bar{2}1$	20 $\bar{2}1$	30 $\bar{3}1$	30 $\bar{3}1$	40 $\bar{4}1$	60 $\bar{6}1$

Letter	<i>s</i>	<i>L</i>	<i>I</i> *	<i>r</i> *	<i>f</i>	\bar{f}	\mathfrak{N}
Symb. Gt. <i>pg</i> ..	1	+1 $\frac{1}{2}$	+1 $\frac{1}{2}$	$-\frac{1}{2}1$	$-\frac{1}{2}1$	-21	$-\frac{1}{2}1$
— Bravais .	11 $\bar{2}1$	32 $\bar{5}3$	7 \cdot 6 \cdot 13 \cdot 7	43 $\bar{7}3$	32 $\bar{5}2$	21 $\bar{3}1$	7 \cdot 3 \cdot 10 \cdot 3

Of these forms those marked with an asterisk are new for quartz.

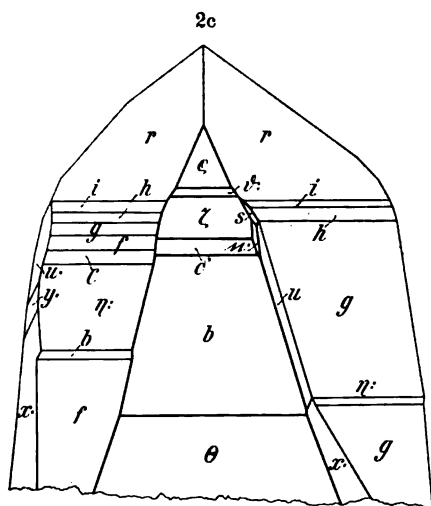
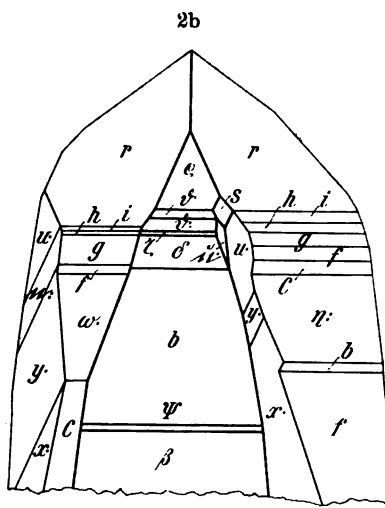
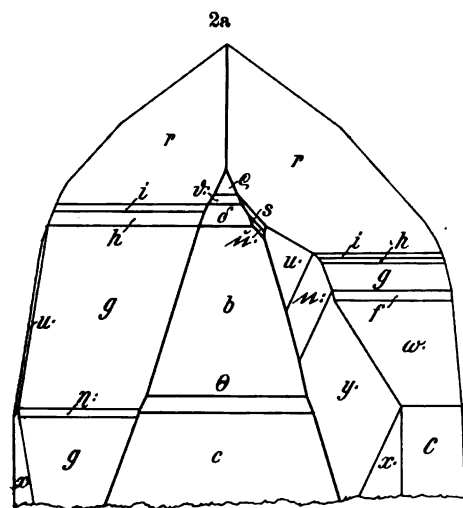
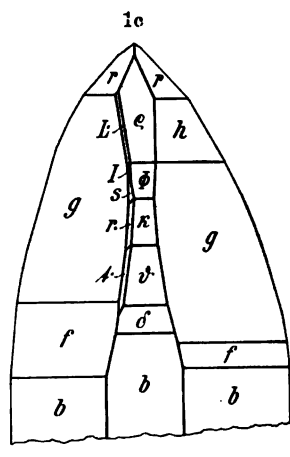
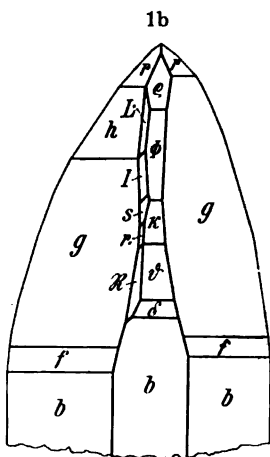
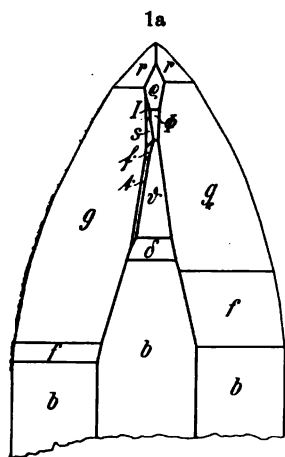
$\phi = -\frac{1}{2}0$ (9097) is represented by three good faces. Measured and calculated values are in close agreement.

Measured $\phi\rho = 0^{\circ}05'$; $58^{\circ}37'$ Calculated $\phi\rho = 0^{\circ}00'$; $58^{\circ}31'$
 $0^{\circ}10'$; $58^{\circ}28'$
 $0^{\circ}01'$; $58^{\circ}35'$

The form may be accepted as certain.

* Published by permission of the Secretary of the Smithsonian Institution.

† *Zeitschr. Kryst.* vol. x, pp. 156-173, 1885. See also Hidden & Washington, this Journal, vol. xxxiii, p. 507, 1887, and Miers, *ibid.*, vol. xlv, pp. 420-424, 1893. Etch-figures on quartz from this locality have been described by Molengraaff, *Zeitschr. Kryst.* vol. xvii, pp. 167-176, 1890.



$I = +1\frac{1}{2}$ ($7\cdot6\cdot\bar{1}3\cdot7$) appears with 3 well developed faces. Measurement and calculations agree well.

Measured $\phi\rho = 27^\circ 30'$; $63^\circ 57'$ Calculated $\phi\rho = 27^\circ 27'$; $63^\circ 56'$
 $27^\circ 45'$; $64^\circ 08'$
 $27^\circ 29'$; $63^\circ 58'$

The form may be considered as established.

$r = -\frac{4}{3}1$ ($\bar{1}573$) possesses 2 well developed faces. Measured and calculated values agree closely.

Measured $\phi\rho = 25^\circ 13'$; $68^\circ 43'$ Calculated $\phi\rho = 25^\circ 17'$; $68^\circ 47'$
 $24^\circ 56'$; $68^\circ 59'$

This form may also be accepted as certain.

From an attempted discussion of the new forms according to their number series,* it appeared that their relations were not clear, due to the uncertainty of many published symbols. The latter are often questionable, not only numerically, but also in respect to their + or - character. Clearness in this direction can only be attained by a critical revision of quartz, following a long series of observations on good material.

CRYSTAL 2. (Collection of V. Goldschmidt.) Dimensions: $10 \times 18^{\text{mm}}$. *Left-handed*. Figs. 2a, 2b, 2c, show the crystal from three sides in natural development. The distribution of the faces appear in the gnomonic projection (fig. 4). The forms identified are shown in the following table:

Letter.....	<i>b</i>	<i>r</i>	<i>p</i>	<i>i</i>	<i>h</i>	<i>ω</i> *	<i>g</i>	<i>θ</i>
Symb. Gt. <i>pq</i>	$\infty 0$	+10	-10	$+\frac{1}{2}0$	+20	$+\frac{1}{2}0$	+30	-30
— Bravais	10 $\bar{1}0$	10 $\bar{1}1$	1011	5053	20 $\bar{2}1$	5052	30 $\bar{3}1$	3031
Letter.....	<i>θ</i> *	<i>θ</i> *	<i>η</i> *	<i>f</i>	<i>ζ</i>	<i>c</i>	<i>C</i>	<i>β</i>
Symb. Gt. <i>pq</i>	$+\frac{1}{3}0$	$-\frac{1}{3}0$	$+\frac{1}{2}0$	+40	-40	+60	+70	-70
— Bravais	10 \cdot 0 \cdot 10 \cdot 3	10 \cdot 0 \cdot 10 \cdot 3	70 $\bar{7}2$	40 $\bar{4}1$	4041	60 $\bar{6}1$	70 $\bar{7}1$	7071
Letter.....	<i>ψ</i>	<i>s</i>	<i>u</i>	<i>u</i>	<i>n</i> *	<i>n</i> *	<i>r</i>	<i>x</i>
Symb. Gt. <i>pq</i>	-11 \cdot 0	1	+31	-31	$+\frac{1}{3}01$	$-\frac{1}{3}01$	+41	-51
— Bravais	11 \cdot 0 \cdot 11 \cdot 1	11 $\bar{2}1$	31 $\bar{4}1$	3141	10 \cdot 3 \cdot 13 \cdot 3	10 \cdot 3 \cdot 13 \cdot 3	41 $\bar{5}1$	51 $\bar{6}1$

Of these forms, those designated with an asterisk are new for quartz. They are well established through their measurements, as follows:

* See Zeitschr. Kryst., vol. xxviii, pp. 1-35, 414-451, 1897.

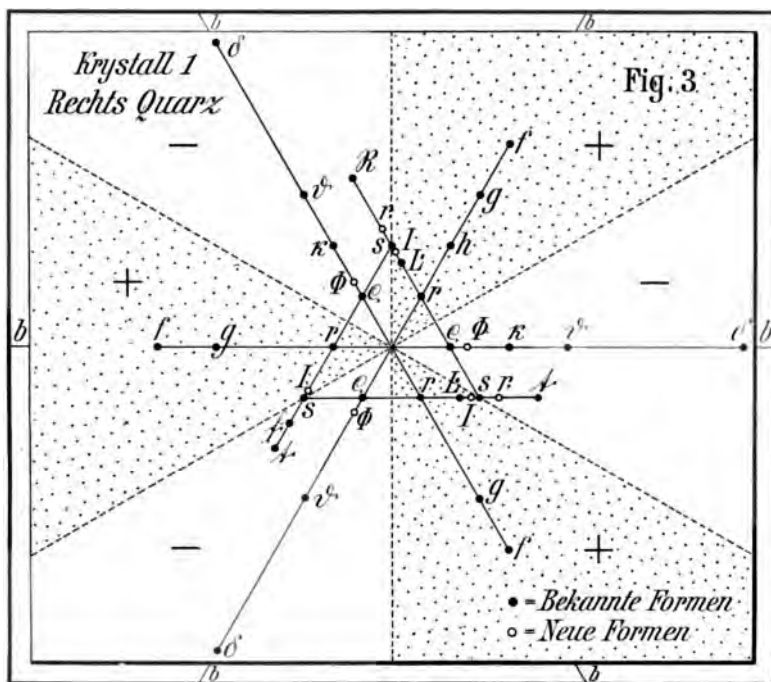


FIG. 3. Gnomonic projection of crystal 1 (right-handed).

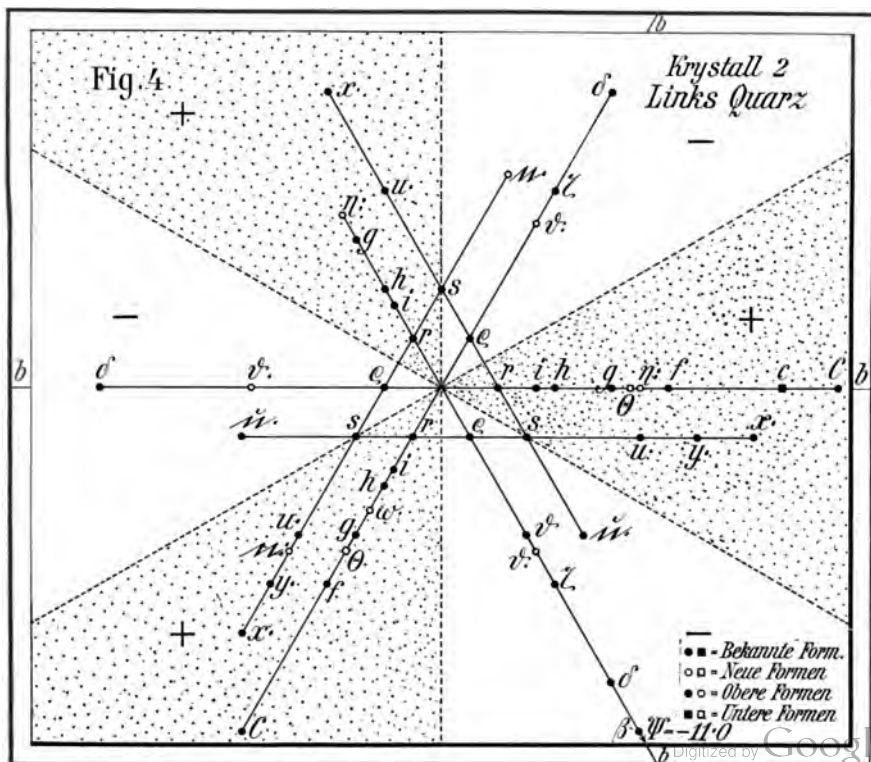


FIG. 3. Gnomonic projection of crystal 2 (left-handed.)

	Measured	Calculated
$\omega. = +\frac{1}{3}0$ with 1 good face, $\phi\rho = 0^\circ 02' ; 72^\circ 53'$		$0^\circ 00' ; 72^\circ 31'$
$\theta = +\frac{1}{3}0$ with 2 good faces, $\phi\rho = 0\ 11 ; 76\ 24$		$0\ 00 ; 76\ 42$
	$0\ 03 ; 76\ 44$	
$\theta. = -\frac{1}{3}0$ with 3 good faces, $\phi\rho = 0\ 03 ; 76\ 47$		$0\ 00 ; 76\ 42$
	$0\ 04 ; 76\ 46$	
	$0\ 04 ; 76\ 54$	
$\eta: = +\frac{1}{2}0$ with 2 good faces, $\phi\rho = 0\ 21 ; 77\ 11$		$0\ 00 ; 77\ 19$
	$0\ 04 ; 77\ 11$	
$n: = +\frac{1}{3}0$ with 1 good face, $\phi\rho = 13\ 03 ; 78\ 32$		$12\ 44 ; 78\ 40$
$n. = -\frac{1}{3}0$ with 1 good face, $\phi\rho = 12\ 53 ; 78\ 44$		$12\ 44 ; 78\ 40$

A discussion of the new forms according to their number series* follows:

For $\omega. = +\frac{1}{3}0$ we have the zone section :

Letter.....	r	i	h		$\omega.$	g
Symb. $pq = 10$		$\frac{1}{3}0$	20	($\frac{1}{3}0$)	$\frac{1}{3}0$	30
$p-1 = 0$		$\frac{2}{3}$	1	($\frac{1}{3}$)	$\frac{1}{3}$	2
$\frac{v}{2-v} = 0$		$\frac{1}{2}$	1	(2)	3	∞

$+\frac{1}{3}0$ passes well in the series. $+\frac{1}{3}0$, not yet noted, is to be expected.

$\bar{\theta} = +\frac{1}{3}0$ and $\eta: = +\frac{1}{2}0$ belong to the zone section :

Letter.....	g	θ	$\eta:$	D	f
Symbol $pq = +30$		$+\frac{1}{3}0$	$+\frac{1}{2}0$	$+\frac{1}{4}0$	$+40$
$p-3 = 0$		$\frac{1}{3}$	$\frac{1}{2}$	$\frac{3}{4}$	1
$\frac{v}{1-v} = 0$		$\frac{1}{2}$	1	3	∞

$+\frac{1}{3}0$ and $+\frac{1}{2}0$ therefore hold a proper place in the series.

For $\theta. = -\frac{1}{3}0$, the following relations appear :

Letter.....	θ	Γ	$\theta.$	η	ζ
Symbol $pq = -30$		$-\frac{2}{3}0$	$-\frac{1}{3}0$	$-\frac{1}{2}0$	-40
$3-p = 0$		$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	1
$\frac{v}{1-v} = 0$		$\frac{2}{3}$	$\frac{1}{3}$	1	∞

The new form $-\frac{1}{3}0$ is in accord with the series, which, however, is not the case with $-\frac{2}{3}0$. The latter was given by Des Cloiseaux† as $et\bar{h}$, and by Rath‡ as $-\frac{2}{3}R$. Their measurements, however, agree rather with $-\frac{1}{3}0$, as the following tabulation will show :

* For explanation of such a discussion consult Zeitschr. Kryst., vol. xxviii, pp. 1-35 ; 414-451, 1897.

† Mém. sur la cryst. et la struct. int. du Quartz. Paris, 1858. Pp. 418-432 ; 528.

‡ Zeitschr. Kryst., vol. x, p. 159, 1885.

Measured—Des Cloizeaux (p. 528); $e\frac{1}{2} : e\frac{1}{3} = -10 : -\frac{2}{7}0 = 24^\circ 49'$
 Rath (p. 159); $-R : -\frac{2}{7}R = -10 : -\frac{2}{7}0 = 25\ 03 - 24^\circ 55'$
 Calculated for $-10 : -\frac{1}{3}0 = 24\ 55$
 Calculated for $-10 : -\frac{2}{7}0 = 24\ 46$

Therefore $-\frac{1}{3}0$ appears as certain; $-\frac{2}{7}0$ as questionable.

$n : = +\frac{1}{3}1$ belongs to the following zone section :

Letter.....	u.	n:	y.
Symbol $pq = +31$	$+\frac{1}{3}1$	$+\frac{1}{3}1$	$+41$
$p-3 = 0$	$\frac{1}{3}$	$\frac{1}{3}$	1
$\frac{v}{1-v} = 0$	$\frac{1}{2}$	$\frac{1}{2}$	∞

Therefore $+\frac{1}{3}1$ passes well in the series.

For $n' = -\frac{1}{3}1$ we have the following :

Letter.....	u'	n'	z'	y'
Symbol $pq = -31$	$-\frac{1}{3}1$	$-\frac{1}{3}1$	$-\frac{7}{3}1$	-41
$3-p = 0$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	1
$\frac{v}{1-v} = 0$	$\frac{1}{2}$	$\frac{1}{2}$	1	∞

$-\frac{1}{3}1$ also passes well in the series.

The positive and negative rhombohedrons ($+10$ and -10) were determined by etching with hydrofluoric acid, and to avoid injuring the specimens the following procedure was adopted.

Crystal 1 belonged to a series of crystals of such similar development that, without danger of error, one of the others was employed for etching. Crystal 2 not permitting of such determination by analogy, the six rhombohedron faces ± 10 were accurately cut upon its lower, undeveloped end, by the aid of a grinding goniometer.* These artificially developed faces were then etched in the ordinary way, the natural faces being protected by a coating obtained by dipping the upper portion of the crystal in a mixture of molten sulphur and fluor-spar. Such a melt was used for a similar purpose by Ph. Hochschild† in a recent investigation on sphalerite.

It finally remained to determine optically the right- and left-handed character of the two crystals by observing the nature of the light rotation in basal section. This was effected with-

* The description of this apparatus has not yet been published.

† Neues Jahrb. f. Min., etc., Beilage-Band, vol. xxvi, pp. 209-210, 1908.

out further harm to the specimens by the aid of the same grinding goniometer; whereby an oriented plane parallel to the base was prepared upon the lower end of each crystal, yielding when sliced off and polished an accurate basal section, examinable under the microscope.

Crystal 1 showed itself as *right-handed* quartz; crystal 2 as *left-handed* quartz. This determination is in agreement with the rule* that the nature of light rotation in quartz may be deduced from the relative positions of the trapezohedrons. Thus, in *right-handed* quartz the trapezohedron faces, both + and -, lie to the right of +10; and reversely, for *left-handed* quartz, the trapezohedron faces are to the left of +10. These relations for each crystal are clearly brought out in the gnomonic projections (figs. 3 and 4).

U. S. National Museum, Washington, and
Heidelberg, Germany.

* See Des Cloizeaux, *Manuel de Minéralogie*, Paris, 1862, vol. i, p. 15.

ART. XXXVIII.—*A Palm from the Upper Cretaceous of New Jersey*; by NEIL E. STEVENS.

THE silicified palm stump which forms the basis of the present study was presented to the Peabody Museum of Yale University by Mr. R. W. Deforest in 1893. But it received no special examination for some ten years, when Dr. G. R. Wieland made several sections from the roots. These sections showed that the structure was unusually well conserved, and

FIG. 1.



FIG. 1. *Palmoxyton anchorus*. Lateral view of entire specimen. $\times 2/5$. Photograph by G. E. Nichols.

finally in the spring of 1911 the specimen was, at Dr. Wieland's suggestion, turned over to the writer for definite study. The various additional sections made by the writer for this study have been deposited, together with the original sections and the type, in the Paleobotanic Collections of Peabody Museum.

The fossil was found by Mr. Deforest on the beach at Seabright, not far from Sandy Hook, and comes accordingly from near the limit of the Upper Cretaceous outcrops on the Jersey Shore. Other specimens, in less perfect preservation, were seen, though the present specimen is the only one so far recovered. The matrix appears to have been a marl, or perhaps clay with little or no lime. This specimen (fig. 1) consists of the much-eroded base of the trunk of a large palm with

the proximal portions of the heavy and dense clump of attached roots. Whether most of the wear preceded silicification or not must of course be largely a matter of conjecture.

Stem.

As will be seen from figs. 1 and 2, comparatively little of the once large stem remains and, on the whole, the preservation of the stem parts is not nearly so good as that of the roots.

FIG. 2.



FIG. 2. Longitudinal section of specimen near the middle, showing crowded roots and small amount of wood. $\times 2/5$. Photograph by G. E. Nichols.

The latter are in an almost perfect state of preservation, far exceeding that of any fossil palm roots hitherto described. This circumstance, together with the fact that fossil palm roots have so rarely been found and have not been very fully described, made a rather careful study of the anatomy of this specimen seem worth while.

In the following paper no attempt is made to review the literature either on fossil palms or on the anatomy of palm roots, as both subjects have been treated at length in recent monographs. Stenzel* describes sixty-two species of fossil palm

* Stenzel, K. G.—Fossilen Palmenohölzer. Beiträge zur Paläontologie und Geologie Österreich-Ungarns und des Orients, Band XVI, Heft IV, p. 1-182, 1904.

woods and four species of fossil palm roots, while Drabble* has studied the root anatomy in a large number of living species of palm. These papers give full citations of the literature in their respective fields.

The maximum height of the specimen (cf. figs. 1 and 2) is 15^{cm}, its breadth 23^{cm}, its length 28^{cm}, and only a small portion of the base of the stem remains, most of which is less well preserved than the roots. Consequently the amount of material from which stem sections could be made was not large. More-

FIG. 3.

FIG. 4.

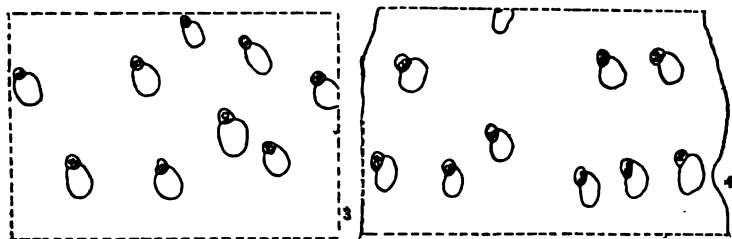


FIG. 3. Outline showing relative size and arrangement of vascular bundles in the inner portion of the stem. $\times 5$. The bundle shown in fig. 5 was taken from this slide.

FIG. 4. Outline showing relative size and arrangement of vascular bundles in the outer portion of the stem. $\times 5$. The bundles shown in figs. 6 and 7 were taken from this slide.

over, in this basal region of the stem the course of the bundles is considerably disturbed, so that any section cuts comparatively few bundles at right angles. However, several small sections were obtained with the parenchyma of the stem and the lignified portions of the fibrovascular bundles in a good state of preservation. The fact that none of the bundles retain their phloem elements is perchance accounted for by the presence of numerous fungus hyphæ.

The parenchyma of the stem shows no unusual features, and there are no bast strands between the vascular bundles, so that in Unger's classification this species would belong to the second great group. Stenzel, however (p. 43), points out that this method of classification is unsatisfactory, and substitutes a system based chiefly on a comparison of the arrangement, proximity, structure, and size of the bundles in the outer and inner regions of the stem; and on the shape and size of the sclerenchyma portion of the fibrovascular bundles.

In our specimen no marked difference could be detected between the inner and outer bundles (compare figs. 3 and 4),

* Drabble, Eric—On the Anatomy of the Roots of Palms. *Transactions of the Linnean Society, Second Series—Botany*, vol. vi, p. 427-487, 1905.

so it apparently belongs in Stenzel's class C.,—the "Cocoa resembling stems." Again, from the shape of the sclerenchyma portion of the fibrovascular bundles it should be placed in the group "Reniformia" (p. 215), which is characterized by having the sclerenchyma portion of the fibrovascular bundle round or oval in cross section with a flat even surface or broad shallow indentation where it joins the vascular portion. This specimen does not, however, very closely resemble any one of the five species ascribed to the "Reniformia."

A typical stem bundle, that is one of the "longitudinal bundles," is characterized (fig. 5) by having in the xylem few but rather large vessels with thick walls. As shown in the figure, the sclerenchyma portion of the bundle is nearly oval in outline with a very slight indentation where it joins the vascular portion. The sclerenchyma cells near the phloem are considerably smaller than those farther away. No sclerenchyma fibers are present on the axial side of the vascular bundle. The parenchyma cells adjoining the bundles are somewhat smaller than those in the remainder of the stem, and the majority of those adjoining the vascular portion are somewhat elongated with the long axis perpendicular to the surface of the bundle.

Besides the longitudinal bundles, a few bundles were found which apparently belong to the classes designated by Stenzel as "Übergangsbündel" or "transition bundles," and "Kreuzungsbündel" or "oblique bundles." By a "transition bundle" Stenzel (p. 139) refers to the region where a bundle that goes up through the stem, that is a longitudinal bundle, turns to go out into a leaf. In this transition region the structure resembles somewhat that of a bundle going out into a leaf. Stenzel* describes bundles of this type as follows: "The bast region is often smaller while the vascular region is larger; the peripheral vessels (that is those nearest the phloem) are more widely separated and often more numerous, while in place of median vessels we find two or more lateral ones. This type of bundle is especially distinguished by the presence of numerous smaller vessels which are found chiefly toward the axial side of the vascular region."

It will be noted that the bundle shown in fig. 6 agrees very closely with Stenzel's description of a "transition bundle," although the sclerenchyma region is not markedly smaller than in the longitudinal bundles. This bundle, which is typical of several found in the sections examined, resembles very closely the transition bundles of *Palmoxylon Aschersoni*. (See Stenzel, p. 140, fig. 234.)

By the "Kreuzungsbündel" Stenzel means those bundles which lead out toward a leaf and so are inclined at a very

* Loc. cit. 1, p. 139.

slight angle. They may also be designated as "oblique bundles." The structure of oblique bundles, according to Stenzel (p. 140), differs from that of longitudinal bundles as follows: "The bast portion of oblique bundles is similar to that of the longitudinal bundles, though very often smaller. The vascular region is much larger and prolonged inwards. Axially to the large peripheral vessels (those nearest the phloem) and separated from them by a region or zone of parenchyma, is a

FIG. 5.

FIG. 6.

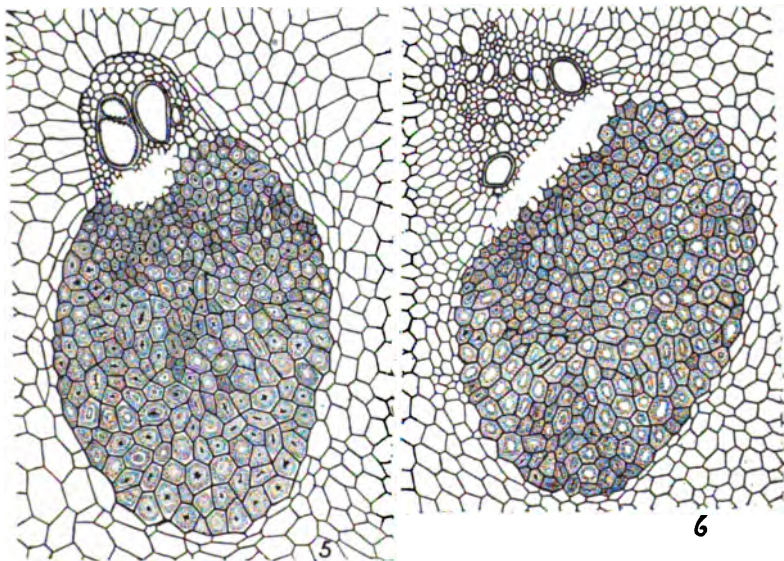


FIG. 5. A typical "longitudinal" bundle of the stem, showing the bast region and xylem containing two large vessels. $\times 65$.

FIG. 6. A "transition" bundle showing the bast region and the xylem containing two large lateral vessels and numerous smaller ones. $\times 65$.

group of numerous smaller vessels. The anterior (peripheral) vessels occur either in two lateral groups or are arranged in a cross row broken up by small "rays of parenchyma." Stenzel divides the oblique bundles into two classes on the basis of the arrangement of their peripheral vessels: group A having "Zwei seitliche vordere Gefässgruppen," and group B "Vordere Gefässe in einer Querreihe." The bundle shown in fig. 7 evidently belongs to the second of these classes and, among the species figured by Stenzel, most closely resembles *P. astorn* (p. 142, fig. 50). The vessels of the xylem present no notable features;

those found in longitudinal section being typical spiral vessels with the coils fairly thick and rather close together.

Tyloses.—One of the most interesting observations is that of the presence in the vessels of both stem and roots of rounded, rather thin-walled bodies which strongly resemble the tyloses of living plants. There is, of course, a bare possibility that these bodies are accretions of some sort, but they are so constant in their appearance and so characteristic in their structure that the conclusion that they are tyloses seems unavoidable. Figure 8 shows a portion of a longitudinal section of a stem vessel which contains several tyloses: fig. 9 shows the tyloses in one of the vessels of a root bundle. So far as the writer has been able to determine, tyloses have not been described in any species of fossil palm. They have, however, been observed in the wood of living palms.*

While the amount of wood available for examination was, to be sure, not large, tyloses were apparently more frequent in the vessels of the root than in those of the stem. This is more noteworthy since tyloses do not appear to have been recorded in living palm roots. They have, however, been found to occur in large numbers in the roots of some herbaceous plants (DeBary); while Chrysler† found them occurring in the heart of the root, as well as in the first growth of the axis of the ovulate strobilus in *Pinus*.

Fungi.—As noted above, no stem bundles were found in which the phloem was preserved. Moreover, only a very small amount of phloem was found in the roots. This may be due, of course, to poor preservation, but it seems more reasonable to attribute it to the action of a wood-destroying fungus, which appears to be present.

It is very difficult to represent satisfactorily on a flat surface the course of the fungus hyphæ, but figs. 10 and 11 give some idea of the number of hyphæ present in many of the vessels of the stem and roots. Hyphæ were equally abundant in the phloem. That this is the mycelium of a parasitic or saprophytic fungus seems reasonably certain since it is confined entirely to the central cylinder, and particularly to the vascular portions; while not the slightest trace of it is found in the cortex. If it were mycorrhiza, of course exactly the reverse would be the case. Hyphæ are rather abundant in the stem, noted above as less well preserved than the roots,—a condition which perhaps suggests that the fungus first infected the trunk and

* De Bary, A.—*Comparative Anatomy of Phanerogams and Ferns*. English edition, Oxford, 1884 (p. 171).

† Chrysler, M. A.—Tyloses in tracheids of conifers. *New Phytologist*, 7: 198, 1908.

later spread to the roots. In fact, as shown below, the cortical portions of the root were in an unusual state of preservation, which might indicate that infection of the roots had taken place only a comparatively short time before silicification.

That abundant hyphæ of a wood-destroying fungus should be found in tissue apparently very little injured is quite in accord with the mode of growth of these fungi. The writer has observed that *Polystictus versicolor*, growing in pure cul-

FIGS. 7-11.

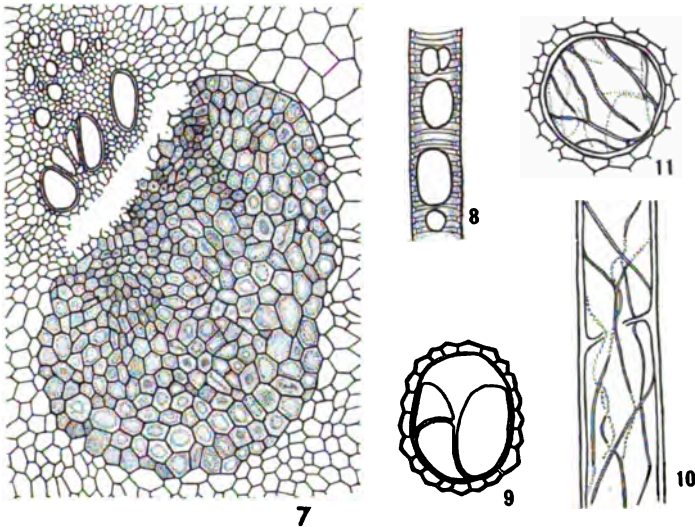


FIG. 7. An "oblique" bundle showing the bast region and the xylem containing large peripheral vessels and a group of numerous smaller vessels separated from the large ones by a zone of parenchyma. $\times 65$.

FIG. 8. Longitudinal section of a portion of a small stem-vessel, showing tyloses. $\times 150$.

FIG. 9. Cross section of a root vessel, showing tyloses. $\times 150$.

FIG. 10. Longitudinal section of a portion of a stem-vessel, showing fungus hyphæ. $\times 150$.

FIG. 11. Cross section of a root vessel showing fungus hyphæ. $\times 150$.

ture on sapwood of *Liriodendron tulipifera*, develops a considerable mycelium extending through most of the woody tissue long before any marked effect on the lignified walls is apparent under the microscope. The fossil fungus noted here had apparently reached just this stage, having developed a considerable mycelium and destroyed much of the phloem, without affecting to any extent the more resistant tissues of the vessels and sclerenchyma.

The Root.

A cross section of the root clump shows the roots closely packed together with but little space between them for some distance below their insertion. The fully developed roots, that is the large ones, are usually somewhat oval in section and about 8 or 9^{mm} by 5 or 6^{mm} in diameter. Figure 12 shows a

FIG. 12.



FIG. 12. Polished surface cut through root clump at right angles to the roots about one inch below the region of insertion, showing marked variation in the size of the closely packed and appressed roots. $\times 4/5$.

number of these roots as they appear in section. The stele of the larger roots is about 2^{mm} in diameter. The numerous smaller roots vary in size down to one millimeter or less in diameter. It is, of course, impossible to determine in a section whether any particular root arises directly from the stem or is a branch of a larger root; but it is evident from the longitudinal sections that branching of the roots is frequent. So it seems probable that a large part of the smaller roots are branches of larger ones.

Cortex.—Drabble (p. 432) divides the cortex of living palm roots into four well-differentiated regions, viz.: (1) outer limiting layer, (2) outer cortex, (3) inner cortex, and (4) endodermis. These four regions are described by Drabble as

follows: The *outer limiting layer* is composed of cells with cuticularized, comparatively thin, walls. It does not necessarily form a perfectly regular sheath. The *outer cortex* (p. 432) is a tegumentary system consisting of several layers of elongated, lignified, and more or less pitted cells. The *inner cortex* (p. 434) is composed of three "zones"; an outer zone usually without air spaces, a broad middle zone with large air spaces, and an internal zone of regular cells. The middle zone

FIG. 13.

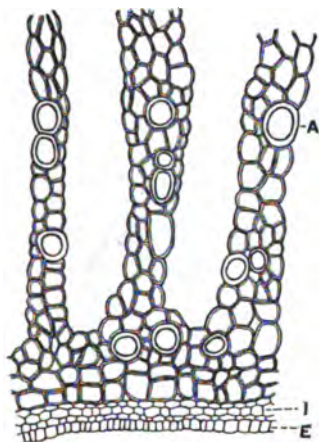


FIG. 14.

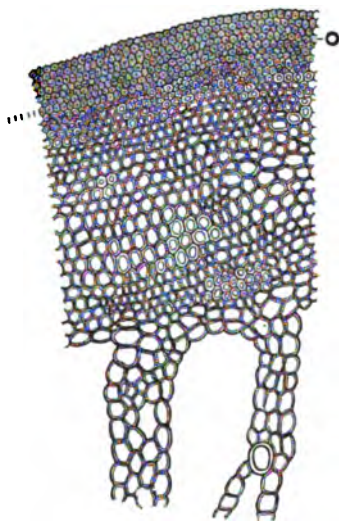


FIG. 13. Inner portion of cortex of large root, showing endodermis (E), and part of the inner cortex, the inner zone of which (I) is composed of three layers of thin-walled cells. In the middle zone of the inner cortex are shown large intercellular spaces and the heavier lignified stone cells (A). $\times 70$.

FIG. 14. Outer portion of cortex of same root as shown in fig. 13, showing outer cortex (O shaded), outer zone of inner cortex, and a portion of the middle zone of the inner cortex. $\times 70$.

shows considerable variation in the shape, size, and number of the air spaces as well as in the number of cell layers separating these spaces. The *endodermis* (p. 438) consists of a single layer (sometimes locally doubled) of lignified cells from three to six times as long as they are broad.

With the exception of the "limiting layer" these same regions were readily distinguishable in the present fossil specimen. Figures 13 and 14 were taken from the cortex of a fully developed root, fig. 13 being, of course, the inner and fig. 14 the outer portion. The photomicrograph, fig. 15, will give an idea of the relative size of the various zones of the inner cortex.

The outer cortex consists of from six to ten layers of elongated, lignified cells with very thick walls and small lumen. The outer zone of the inner cortex is also composed of lignified cells, but they are thinner-walled and shorter in proportion to their length. The cells of this region differ considerably in size, the outermost cells having about the same diameter as the adjacent cells of the outer cortex, while toward the center the cells become progressively larger in diameter.

The middle zone of the inner cortex contains numerous large air spaces. These air spaces (lacunæ) are radially arranged, six to ten times as long as broad, with from one to

FIG. 15.

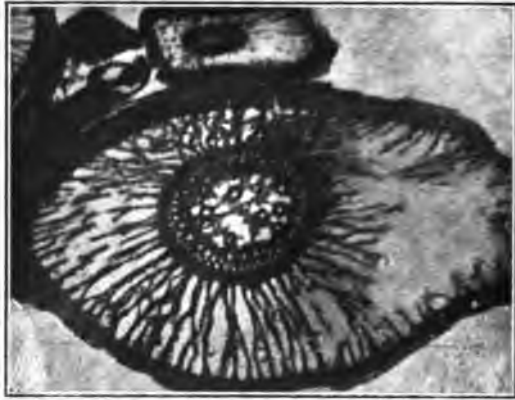


FIG. 15. Photomicrograph of cross section of palm root, showing cortex with large radial intercellular spaces in the middle zone; and stele with alternate phloem and protoxylem groups and eight internal vessels. $\times 8$.

six layers of cells separating them. The cells of this region are only about twice as long as they are broad and much thinner-walled than those of the outer region. In addition to the large radial air spaces, triangular spaces show plainly in the longitudinal section at the intersection of cell walls (fig. 16). The cells are apparently "lignified parenchyma."

There occur also in this middle zone thick-walled cells with large cavity and large pits. These usually occur singly or scattered through the middle zone in groups of two or three, but are somewhat more numerous toward the inside. Seen in cross section, figs. 13 and 14, they usually appear rather round; and in fully developed roots the pits are not usually seen in cross sections. In smaller roots, however (fig. 22), the large pits are very evident. Figure 17 shows two of these

large cells from near the origin of a root, in longitudinal section. It will be noted that these cells are from three to five times as long as they are broad and that the large pits are considerably elongated. It is difficult to place these cells in any of the recognized categories of lignified elements. They do not seem to correspond exactly to either the "Kentia" or "Raphia" types of fibers described by Drabble (p. 435), but may perhaps be designated as "stone" cells.

The internal zone of the inner cortex usually consists of three layers of rather thin-walled cells closely packed together without intercellular spaces. These cells vary considerably in size but are usually from one to three times as long as they are broad. Compare fig. 13 with fig. 16.

The endodermis is almost uniformly one cell thick, the cells two to four times as long as broad; and even in the fossil the radial walls appear markedly thicker than the tangential walls. Compare fig. 13 with fig. 16.

All the regions described for the fully developed root can be made out in the smaller root shown in fig. 22. In the smaller root, however, the various parts of the inner cortex are not so clearly differentiated and all the cells have much thinner walls.

Nuclei in cells of inner cortex.—Three longitudinal sections showed the parenchyma cells of the inner cortex in a very remarkable state of preservation. Indeed, the majority of the cells of this region contained structure so characteristic in appearance and so constant in occurrence that, if seen in fixed material from living plant tissue, they would unhesitatingly be described as the well-stained *nuclei*.

Drawings of such structures would naturally afford no certainty as to their nature; and the photomicrographs, figs. 18 and 19, are accordingly offered for what they may be worth as proof. While not fully convincing in themselves these figures are not wholly valueless. Practically every parenchyma cell in the field showed a nucleus in some focus; and in the figures nuclei appear in the cells marked N as well as in some others. It will also be noted that the triangular intercellular spaces spoken of above clearly appear in these photomicrographs; and the probability of the cells having been "fixed" when in an actively growing condition is further denoted by the occurrence of pairs of cells which have apparently just been separated by a cross wall (*y*, fig. 19). In these "daughter cells" the nuclei are still close to the dividing wall.

The Stele.—The pericycle is very readily distinguished as a single layer, or sometimes locally as two layers, of rather regular cells inside the endodermis. These cells tend to be some-

what larger than the parenchyma cells adjoining them and their radial walls are for the most part regularly perpendicular to the walls of the endodermal cells. Compare figs. 20, 21, and 23.

The vascular portions show the typical root arrangement, the phloem strands alternating with the protoxylem groups.

FIG. 16.

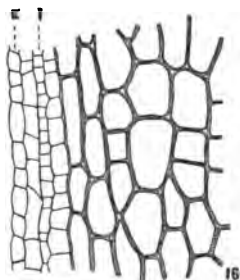


FIG. 17.

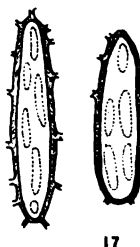


FIG. 16. Longitudinal section of inner region of cortex, showing endodermis (E), and a portion of the inner cortex with lignified parenchyma and inner zone of three layers of cells (I). $\times 112$.

FIG. 17. Two of the large "stone" cells of the inner cortex in longitudinal section, showing large pits. $\times 112$.

FIG. 18.



FIG. 19.



FIGS. 18 and 19. Photomicrographs of parenchyma cells of the inner cortex in longitudinal section, showing nuclei (N) and cells which by their shape seem to indicate recent division (y). Triangular intercellular spaces may be seen in some cases. $\times 100 \pm$.

In the larger roots there are usually fifty or more protoxylem groups; in the root from which fig. 20 was taken there were fifty-five. The phloem groups and all the outer xylem elements are surrounded by a continuous zone of dense sclerenchyma fibers. These sclerenchyma fibers are considerably smaller near the vascular portions than they are toward the center of the root. This dense sclerenchyma band is usually

from fifteen to twenty-five cells wide, so that in the large roots the sclerenchyma region with the vascular portions it contains occupies only about half the stele.

The central portion of the stele contains a variable number of "internal" vessels, frequently from four to six, which do not appear to be referable to any particular xylem group. Compare (Drabble, p. 441). Each of these internal vessels is surrounded by a region of dense sclerenchyma from six to ten cells in width. See fig. 20. The remainder of the central

FIG. 20.

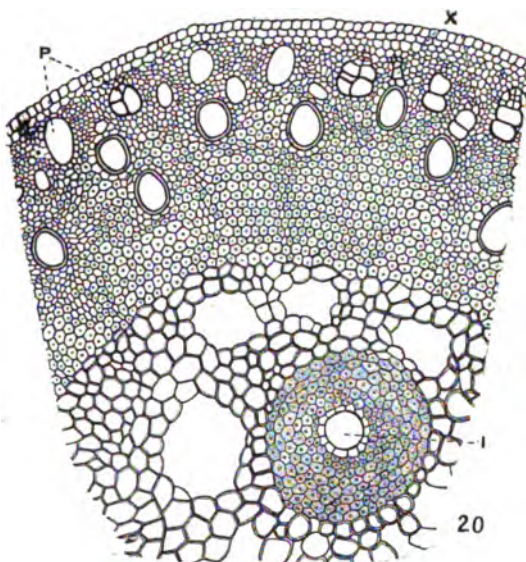


FIG. 20. Portions of stele of large root with endodermis, showing pericycle, alternate phloem (P) and protoxylem (X) groups in a zone of dense sclerenchyma. The inner region of the stele shows lignified parenchyma with large intercellular spaces, and an internal vessel (I) surrounded by a zone of sclerenchyma. $\times 175$.

region of the stele is occupied by lignified cells with large lumen and comparatively thin walls. These cells apparently became torn apart as the root increased in size so that, in fully developed roots, this central region has large intercellular spaces.

The stele of the smaller roots shows the same structure as that of the larger ones, but the number of protoxylem groups is much smaller. The root shown in fig. 21 had thirteen pro-

toylem groups. In these smaller roots, of course, the central region is much smaller in proportion to the whole stele and contains no internal vessels or large intercellular spaces.

One of the most interesting sections found was that of the very small root shown in fig. 23. While no phloem elements can be distinguished in this root section, the xylem shows the arrangement of a very young tetrarch root. In this very small root, as in the larger ones, the pericycle may be readily distinguished. Unfortunately the cortical portion of this root was obscured by a deposit of some foreign substance.

Phloem.—As noted above, the phloem was preserved in comparatively few cases. Not more than five of the root sections

FIGS. 21-24.

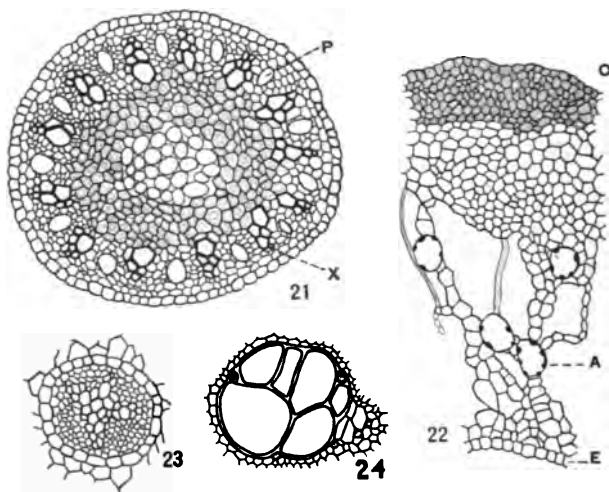


FIG. 21. Stele of a smaller root with endodermis, showing pericycle, alternate phloem and xylem groups, and a zone of sclerenchyma. $\times 175$.

FIG. 22. Cortex of same root as that shown in fig. 21, endodermis (E), stone cells (A), outer cortex (O). $\times 175$.

FIG. 23. Stele of very small root, the xylem of which has the typical tetrarch arrangement. $\times 175$.

FIG. 24. Phloem group from large root. $\times 265$.

showed well preserved phloem. Even in the root shown in fig. 20, less than half of the phloem groups remained. Fig. 24 shows, however, a group which was unusually well preserved, and this may perhaps be taken as typical. It will be noted that the protophloem consists of small cells with thin walls while the sieve-tubes of the metaphloem are very much

larger and have thicker walls. No sieve-plates could be discovered in any of the sections. Neither could companion cells be definitely distinguished. It seems probable, however, that the small dark regions close to the sieve-tubes, shown in fig. 24 by the shaded areas, occupy the position of companion cells. All the preserved phloem groups were in the larger roots.

Junction of bundles of root and stem.—The transition from the solid stem to the root region of variable hardness renders the making of thin sections through the root junctions difficult, the more so because the parenchyma and other tissues in this region have taken on so dark a color that sections of moderate thickness are not very useful. These circumstances prevented satisfactory study of the junction of the root and stem bundles.

Description of species.

***Palmoxylon anchorus*, sp. nov.**

Locality.—Upper Cretaceous, Seabright, New Jersey.

Type in Peabody Museum, Yale University.

Stem.—No bast strands between the fibrovascular bundles. Sclerenchyma portions of the fibrovascular bundles usually oval in cross section and but little indented next the phloem. Little difference in the size and shape of the sclerenchyma portions of the "longitudinal," "transition," and "oblique" bundles.

Roots.—Roots considerably branched. Outer cortex composed of six to ten layers of elongated, lignified cells. Inner cortex differentiated into three zones: an outer region of thick-walled lignified cells; a middle zone of lignified parenchyma having numerous large radially arranged air spaces, six to ten times as long as broad, separated by from one to six layers of cells; and an internal zone of three layers of thin-walled closely packed cells. Endodermis usually one cell thick. Pericycle usually one or locally two layers of cells. The largest roots have over fifty protoxylem groups alternating with phloem groups. Internal vessels present in the larger roots and surrounded by a dense region of sclerenchyma six to ten cells in width.

* * * * *

It is of much interest to append the fact that petrified stems of palms are not the rare objects that their noticeable absence from collections and general lack of mention in paleontologic texts would seem to imply. It is indeed probable that they

occur abundantly at times from the upper Cretaceous on, both on the coastal plain and in the formations of the continental interior.

In addition to several Tertiary forms described by Knowlton, Hatcher is known to have secured various stems from the Laramie of Converse county, Wyoming. Wieland has collected from the Pierre the splendidly conserved stems arbitrarily called by him *Palmoxylon cheyennense*.* Cannon has secured an abundance of exquisitely silicified stems from the Denver beds. And only last year Brown observed a large silicified root clump in the "Rattlesnake" beds on the "big bend" of the Rio Grande in Chisos county, Texas.

* This Journal, vol. xv, p. 216.

ART. XXXIX.—*Preliminary Note on the Shower of Meteoric Stones near Holbrook, Navajo County, Arizona, July 19th, 1912, including a Reference to the Perseid Swarm of Meteors visible from July 11th to August 22d*; by WARREN M. FOOTE.

History.

It was doubtless the literary exaggerations of the 18th century and similar causes which prevented early geologists and astronomers from investigating the reports of falling sky-stones. But in the fatherland of yellow journalism we sometimes find a journalistic restraint, under conditions that are worthy of remark, and which prove the labor of the news-gatherer to be of value to science. In the last week of July, the following account appeared in several Arizona papers:

Friday evening about six-thirty a meteor, or some other body of a like nature, passed over Holbrook going almost due east at a rate of speed that would make a swift-moving express train seem as though it were standing dead still. The noise it created was very loud and lasted for at least a half a minute and sounded somewhat like distant thunder or the booming of a cannon in the distance. It left a large cloud of smoke in its trail and several of our citizens heard it explode a couple of times. A few saw it and nearly everyone heard the noise it made. Reports from Winslow are that several people saw the body pass over the town, and the noise was heard at St. Joseph, Woodruff, Pinedale, and Concho. That either all or part of the body fell near the section house at Aztec, six miles east of here, there seems to be little doubt.

* * * *

A few small pieces were brought in here. One piece larger than an orange fell into a tree in a yard at Aztec cutting the limb off slick and clean and falling to the ground, and when picked up was almost red-hot. Other particles of the body fell in the same vicinity and an eye-witness states that for about a mile to the east he could see little puffs of dust arising from the sand, evidently where fragments struck.

* * * *

About two dozen people went to Aztec to pick up pieces of the meteor Sunday afternoon and the field is now pretty well cleaned up. The largest found weighed over 14 pounds, while several of about 5 pounds were picked up, and numerous small pieces. They are very brittle, heavy, and appear to have many small particles of iron in them.

As the writer of the present article lacked the time for making the two-thousand mile journey from Philadelphia, the additional and confirmatory data were secured by correspond-

ence with witnesses of the fall and with finders of the stones. Following are the main facts of the fall and find, as gathered.

Between 6.20 and 6.40 p. m. on July 19th, 1912, a large meteor was heard traveling in an easterly direction and passing over Winslow, Holbrook, and Aztec, points along the Santa Fe Railroad, which here parallels the Rio Puerco River. It made a very loud noise, lasting for half a minute to one minute.* This noise has been variously likened by witnesses, to the rumbling of a rapidly driven farm wagon on a rough road, to escaping steam, to distant or long continued thunder

FIG. 1.

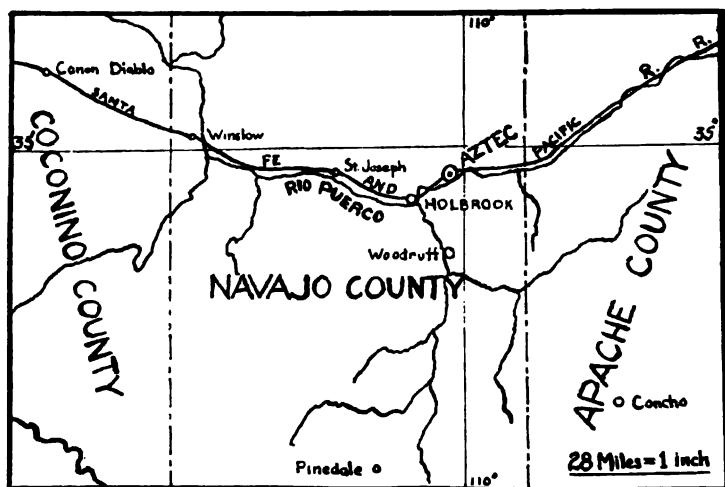
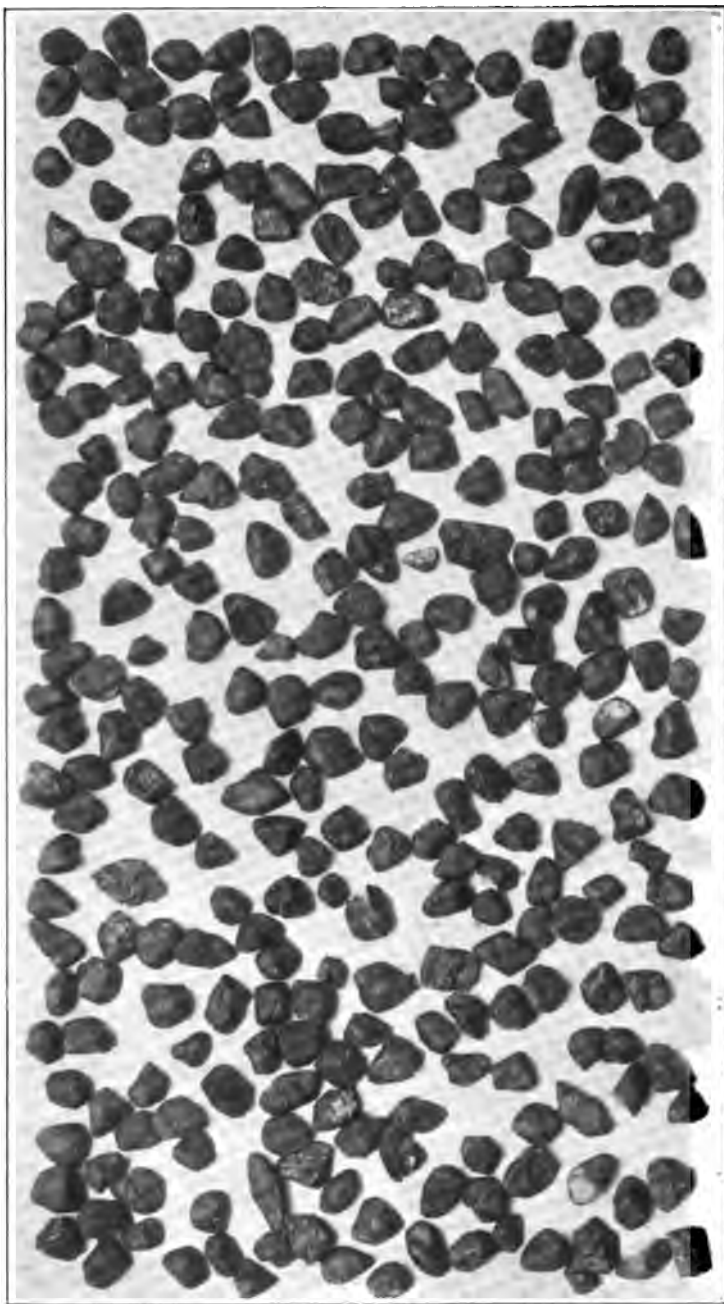


FIG. 1. Location of Fall. Aztec, near Holbrook, Navajo County, Arizona. $34^{\circ} 57' N.$, $110^{\circ} 2' W.$

or the booming of a cannon. It was heard at Concho, St. Joseph and Woodruff and at Pinedale, some forty miles away. One large explosion was quickly followed by several small ones in rapid succession. Charles Von Aachen and his son then saw numerous stones fall at Aztec, raising many puffs of dust for a mile or more over the dry sand of the desert, like those produced by bullets or the first drops of rain in a heavy shower. They did not see the stones in the air. Some fell near a building, and one is said to have severed the branch of a tree. The meteor was not seen during its flight, as it was too early in the evening for its luminosity to be visible. Its speed could not be estimated, but it was "terrific" according to one account. Its

*One observer states that the loud reports were followed by lesser rumblings for four or five minutes. These were the usual echoes.



Photographs by Bond Bros., Philadelphia.

FIG. 2. "Holbrook peas." 360 complete boloids. Full size, about 4 to 8^{mm} long. 0.1 to 0.3 grams or 1.5 to 5 grains. Total weight, 70 grams.

path was indicated to many by a train of thin smoky vapor which spread out after the meteor passed. One observer estimated that the explosion occurred one or two miles above the earth. The weather at the time was slightly cloudy.

The stones were scattered over an ellipsoidal area roughly estimated by two finders to be about one-half mile wide and three miles long. As frequently recorded in meteoric falls, the longest diameter of this ellipsoid was in line with the trajectory of the meteor, being east and west. Most of the

FIG. 3.



FIG. 3. Characteristic pyramidal brustseite, with two rear corners broken and later fused. $\times 1'$ diameters.

smaller fragments lay on the top of the loose sandy soil; the larger pieces were about half buried, some to a depth of six inches, apparently having fallen slantingly from the west. The large and small stones, according to all answers received, were said to be indiscriminately spread over the ground, without regard to size.* In previous stone showers the small stones have been found first in the line of flight, then the medium, and finally the largest. The violent disruptions near Holbrook might account for the lack of such separation of the sizes, provided an explosion occurred near the end of the flight. Just such a late disruption was evidenced by the nearly

*See further, note on p. 456.

fresh fracture of many fragments. Visitors from nearby towns soon gathered the larger stones. Von Achen, who saw them fall, reported that they were too hot to pick up. Two accounts state that they became lighter in color after cooling. Except for about ten kilos sent away, all were acquired by the Foote Mineral Company of Philadelphia.

There is an Aztec post-office in Yuma Co., Arizona, but no post-office or telegraph station at Aztec, Navajo Co. Hence

FIG. 4.



FIG. 4. Specimen three-quarters buried in wet soil, resulting in rust and exudation of molysite. Checked surface exposed. Oblique angle of flight indicated by soil line. $\times 1$ diameters.

the name of *Holbrook*, six miles distant, is used to designate the fall.

Macroscopic Features.

Externally the stones present all the commoner characteristics of aërolites. The primary crust, begun on the entrance of the meteor into our atmosphere with its high planetary velocity, and prior to the first explosion, is almost universally present. It coats broadly rounded surfaces and is generally dull black, being about 0.3mm thick. A checking or crackling of this crust, due to unequal expansion, is often noticeable, as shown in fig. 4. The secondary crust, formed on the fractured surfaces produced by this first disruption, is somewhat shiny

and thinner than the older crust. Moreover, the fractures it covers are hackly and irregular, and it even fails to hide occasional protruding chondrules, indicating that the superficial dissipation by combustion had not proceeded far enough to round off the sharper corners and smaller prominences.

What may be termed a tertiary crust was begun subsequently to the second explosion when nearing the ground at reduced velocity. The genesis of this is most interestingly shown in various stages. A slight discoloration, especially a tarnishing of the metallic minerals, is sometimes seen. A mottled smoking of the surface and an incomplete incrustation of small patches is quite common and grades into a thin filmy crust (see fig. 5).

FIG. 5.



FIG. 5. Primary crust at left. Tertiary crust beginning as a smoky alteration. $\times 0.85$ diameters.

On many of the smaller stones this tertiary crust is fully developed at the edges of the primary crust, being in fact a labiate overflow of the latter. The newly fractured area often shows the various degrees of fusion as its center is approached, where in some cases only a smoky alteration may be seen. Rarely the primary, secondary, and tertiary incrustations are exhibited in the same fragment.

Several dozen individuals showed the characteristic radial flowage lines of viscous stone from the front, or brustseite, to the back. This flow is due to the backward rush of air over the molten surface. It was noted in some pieces of not over

1^{cm} diameter. The most deeply and unusually marked brustseite found was on a large stone of 2,400 grams, shown in figures 6 and 7. The wholly unique character of this piece suggests that it was the front end of the original large mass, or one of several large masses, which entered the earth's atmosphere. Here the lines of flow are merged and sometimes originate in deep pits, or piezoglyphs, probably caused by a

FIG. 6.

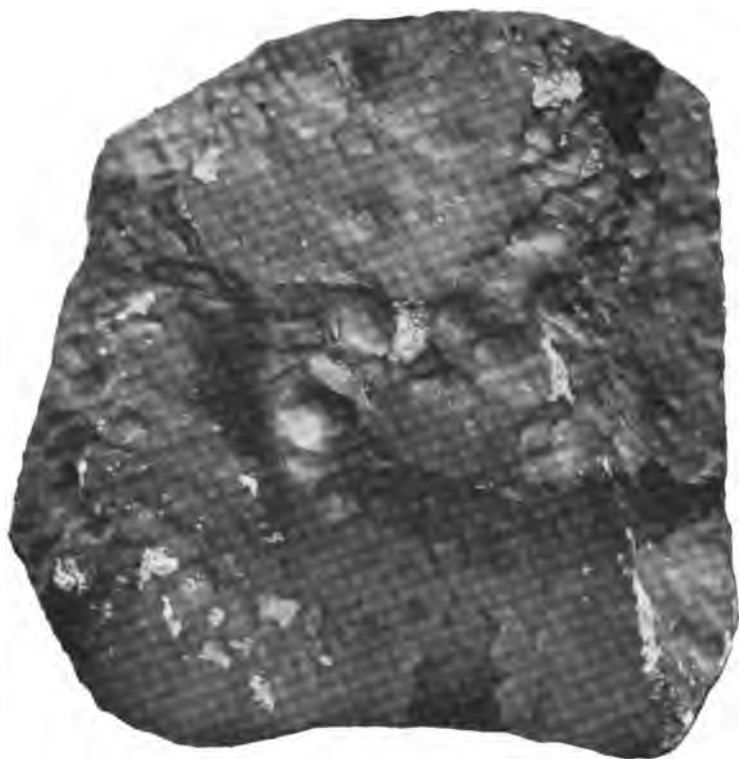


FIG. 6. Brustseite with deeply marked radial fusion flow (reconstructed).
× 0.64 diameters. See also Fig. 7.

differential fusing or fracturing of the surface from heat and very rarely by the burning out of nodules. Unfortunately the finder of this mass treated it with scant respect, and it reached Philadelphia in three fragments scattered among thousands of other stones. The edges were much bruised from rough handling, so that the reconstructed corner and cracks, shown plainly

in the engraving, are comparatively large. The back of the stone (fig. 7) illustrates well the relatively quiet fusion of all of the similarly marked masses. In these the overflow of the molten silicates behind the rear edges is shown sometimes in a fringe-like scoriaceous "wash" or thicker crust. Otherwise

FIG. 7.



FIG. 7. Back of mass shown in fig. 6 (reconstructed). $\times 0.64$ diameters.

the back plainly appears as an area of lesser fusional disturbance than the front.

Several of these specimens are superficially identical with that of Gopalpur, described by Tschermak, as having a rounded front covered with a finely striped and radiately channeled crust, with elongated pit-like depressions, becoming shallower as they recede from the radiant point. Gopalpur's front crust overlaps the back in a well-defined and sometimes fringed border, becoming verrucose and enclosing unaltered grains of

the meteorite. One 450-gram Holbrook fragment with deeply furrowed brustseite similarly shows 1 to 2^{mm} fragments of unaltered stone enclosed in the back crust, the semi-fused area being 1 to 3^{mm} thick.

A few well-marked brustseite stones (fig. 3) show fractures near the base; none at the head of the stone. This would indicate that the pressure of the air stream on the rear edge is a factor in disruption, as well as the expansion due to heat. In some instances the radial fusion flow is shown on the secondary crust of fragments, notably in figs. 8 and 9. Here the stone was apparently reversed in its flight

FIG. 8.



FIG. 9.



FIG. 8. Front of stone, showing radial fusion flow on primary crust.

FIG. 9. Back of same stone, showing flow on secondary crust after reversal of position in flight. $\times 0.9$ diameters.

after an early explosion, and a well-marked radial flow was left upon the new brustseite.

In the examination of a large number of stones, the thick and minutely blebby character of the otherwise even crust on one face would indicate the back of the stone, whereas the fusion flow on the reverse, or front, might be but faintly marked, or even absent. The front is often brownish, the back being usually deep black.

In rare cases the pits clearly result from the burning or fracturing out of pyrrhotite nodules, as illustrated in fig. 10. At the lower end of the pit is a piece of the freshly fractured pyrrhotite. In the bottom of the pit is the smoothly altered slaggy remnant of the original nodule, similar to the unaltered one shown in fig. 13. Some of these inclusions are sharply rectangular and possess a distinct parting. Qualitative tests

show the mineral to be essentially sulphide of iron. It may therefore be provisionally classed as pyrrhotite.

No tendency toward any one fragmental form is observable except that the stones with well-marked fusion flow are generally of a roughly pyramidal or conical shape, the apex corresponding with the radiant point of the fusion lines; the base is the back of the individual in flight.

According to a local account, the rust noticed on a few stones was caused by rain between the falling and finding of the specimens. On these is observable the usual liquid exudation of molybdate (ferric chloride, FeCl_3), the alteration of lawrencite (ferrous

FIG. 10.



FIG. 10. Piezoglyph formed by burning out of pyrrhotite nodule.
x 0.77 diameters.

chloride FeCl_3). The remainder of the thousands of individuals examined seemed to be entirely stable and bear no signs of disintegration. On many pieces are traces of the sandy reddish soil on which they fell. Two or three per cent showed a "soil line" (fig. 12) indicating clearly the depth of burial. A very few showed traces of the soil on all sides. This is, of course, not a reliable indication of the average depth of burial, since the amount of cleaning done by the finders cannot be determined. The direction of this soil line, shown in fig. 4, would indicate that the angle of fall with the earth's surface was about thirty to forty degrees. From the slight penetration of

the soil observed, the last stage of the flight was evidently not incomparable with the velocity of an ordinary falling body, as has been accurately calculated by investigators of previous falls.

The relatively low temperature at the moment of reaching

FIG. 11.



FIG. 11. Flat Brustseite. $\times 0.73$ diameters. See fig. 12.

FIG. 12.



FIG. 12. Flat Brustseite (down). Side view showing confirmatory soil line and scoriaceous overflow on back (up). $\times 0.76$ diameters.

the earth's surface is suggested by one specimen with uncharred vegetable fiber adhering closely to the rough crust. The impact apparently pressed the fibers firmly into the minute interstices of the crust.

Examination of a fractured surface shows a light ashy gray color and the granulated texture imperfectly reproduced in fig. 13. Irregular chondrules, visible to the naked eye, are common, and here and there others become prominent by their spherical form breaking half free from the matrix. In some instances these hemispheres are quite perfect and of four or five millimeters diameter, the largest one, illustrated in fig. 14, reaching 11 millimeters. It has lost much of its definiteness in photographing.

Under a lens, the chondrules breaking with the matrix are seen to be numerous distributed throughout the mass. A

FIG. 18.



FIG. 13. Fractured surface with pyrrhotite nodule. $\times 1$ diameters.

large number of the chondrules are gray in color, others are whitish. Not infrequently a broken chondrule shows radiofoliate structure, sometimes with the radiant point at one edge.

Microscopic Examination.

This was made by Mr. W. Harold Tomlinson, whose report follows:—

The new meteorite is an aërolite containing a very little native iron. There are three opaque minerals forming together perhaps 4 per cent of the volume. Native iron and pyrrhotite

FIG. 14.



FIG. 14. Unusually large spherulitic chondrule, broken freely from the matrix. $\times 1$ diameters.

occur in irregular but usually rounded patches and grains, in about equal amounts. The pyrrhotite occasionally shows crystalline faces. Magnetite in small jet black or slightly bluish black grains occurs to less extent than the other metallic minerals.

FIG. 15.



FIG. 15. Imperfect polish showing distribution of nickel-iron. At large end a chondrule encircled by minute iron grains. $\times 1.7$ diameters.

The principal constituent of the stone is enstatite, which forms probably 50–60 per cent by volume. It occurs in prisms from $1^{\text{mm}} \times .25^{\text{mm}}$ in size down to minute allotriomorphic grains. It also occurs often in chondrules with radiating structure (fig. 17), and in one section a chondrule was found with tangential structure, i. e. the fibers formed a regular polygon. Enstatite appears to have been one of the first minerals to separate and to have continued its separation until the magma cooled. In mass the enstatite has often a slightly greenish color. It is colorless in section.

Olivine and monoclinic pyroxene (diplaxite) make up the balance of the stone. Olivine occurs usually in crystals and crystal grains set in a grayish glass. A group of olivine set in glass will be divided from the rest of the stone often by sharp demarcation as though it were an inclusion of another stone.

Olivine also occurs frequently in less perfect crystals associated with the enstatite, but segregation is rather characteristic of it in this stone.

The diallage in mass is a brownish color. In section it has in some places a very slight pinkish tinge, but is usually colorless. It occurs in grains with few crystal boundaries and in large crystals. One large crystal measured approximately $2.5 \times 2^{\text{mm}}$. It also occurs twinned or intergrown with the enstatite and in some of the chondrules it is twinned with the enstatite. There are some longish prisms with fibrous structure and small extinction angle that are also monoclinic pyroxene.

FIG. 16.

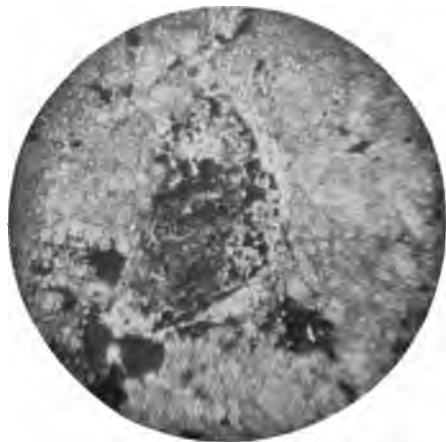


FIG. 16. Sharp octahedrons of spinel in quartz. $\times 30$ diameters.
Lower nicol in place.

The most interesting feature observed was a patch of spinels set in quartz. Of ten sections examined, these minerals were found in only one. They shade in color from clear and rather light ruby-red to ruby-brown. The darker are shining black by reflected light, and are probably chromite. On the light side of the patch the crystals are red by reflected light, and are therefore a ruby- or chrome-spinel (fig. 16). They occur in sharp octahedrons and are the most perfectly crystallized mineral in the stone. They are identified by color, crystal form, reflection, and position. The crystals are set in semi-crystalline quartz and the patch is edged with quartz that is slightly coarser. The granules of quartz are irregular in shape, often interlocking, and show wavy extinction. No figure was obtained beyond an indistinct dot which

had no effect on a quartz wedge. The quartz is sufficiently identified, however, by its low refraction, double-refraction showing colors up to white, and by the characteristic habit of the grains.

These patches of spinel and quartz are analogous to the patches of olivine and glass previously described. The two minerals should probably be regarded as secondary minerals formed by a reaction (perhaps influenced by Cr_2O_3) between the olivine and anorthite or a glass near to anorthite in composition.

Chromite was found in three sections. It occurs associated with the metallic minerals. It is black by reflected light and dull red by transmitted light. Both patches and crystals were found.

FIG. 17.

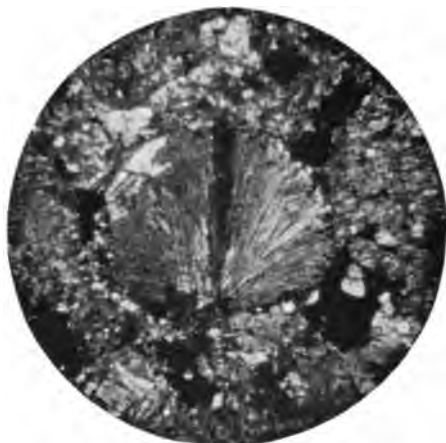


FIG. 17. Chondrule of enstatite surrounded by native iron and pyrrhotite. $\times 16$ diameters. Nicols crossed.

Nickel-Iron Content.

Mr. George C. Davis made the few chemical determinations of the aërolite which limited time permitted. The specific gravity was found to be 3.22. One hundred grams, freed from crust, were finely powdered and treated repeatedly with the electro-magnet. The metallic portion was washed with alcohol to remove the silicates, but the separation was incomplete and the silicates finally constituted about 25 per cent of the magnetic concentrates. The material for analysis was taken from twelve individuals.

Weight magnetic portion,	actual	4.90
Weight non-magnetic portion,	actual	95.
Weight magnetic portion,	corrected....	3.675

The corrected weights give the following percentage for the aërolite:

Nickel-iron	3.68
Silica	96.32
	<hr/>
	100.00

Analysis magnetic concentrates.

Silica	14.12
Iron	60.64
Nickel	11.84

Corrected for 25 per cent non-magnetic minerals present.

Iron	80.86
Nickel	15.79

Astronomical Relationship.

Astronomers have long debated the question as to whether the fall of the Mazapil (Mexico) iron* on Nov. 27th, 1885, proved it to be actually a member of the swarm of Leonids or November meteors seen numerously on the same night, or whether the occurrences were purely coincidental.

The well-known August or Perseid meteors are seen from July 11th to August 22d (Denning), and reach a maximum on August 10th to 13th, while the lesser Aquarids reach their maximum on July 28th. Their nearness suggested an inquiry as to a possible relationship between these star showers and the Holbrook meteorites.

Apprized of the circumstances of the Holbrook fall, Prof. Eric Doolittle, Director of the Flower Observatory, University of Pennsylvania, wrote as follows:—

October 5, 1912.

I was greatly interested in your account of the extraordinary fall of meteoric material in Arizona on the evening of July 19th, last, and I take great pleasure in giving you what information I can regarding the known meteoric showers which may be expected at about this date.

The nearest bright shower in point of time is undoubtedly that known as the Aquarid shower, which reaches its maximum on July

* See this Journal, xxiii, 221, 1885.

28,—but nine days later than the fall observed. Yet I hardly think it possible that the material actually collected can belong to this meteoric stream, for the reason that the region of the sky from which the Aquarids are seen to come had not yet risen above the eastern horizon nor would this region begin to rise until about one hour later. And as at this time the constellation Aquarius would be seen in an almost due easterly direction, it seems not possible that a member of this stream could be seen coming from the west, as the Holbrook meteorite did.

The next brilliant shower in point of time is the well-known Perseid shower, more commonly known as the shower of August shooting stars. Although this shower was most brilliant from August 10th–13th of the present year, the individual particles are so greatly scattered that straggling members may be seen for nearly a month before this date. The point among the stars from which the meteors of this stream are seen to come is constantly changing during this time, owing to our displacement in space caused by the motion of the earth. According to Mr. W. F. Denning,—the highest present authority upon this subject,—the occasional meteors from this shower witnessed on July 19th should apparently come from a point just without the borders of Perseus and within those of the constellation Cassiopeia. At the time under consideration this point of the heavens would be almost exactly in the north horizon, or at most but a degree or two to the west of north. The greater part of the particles which reached us from this stream at this time should therefore be expected to approach our country from the north, and to at least begin their motion through our air in a path very nearly parallel to the ground. However a single, isolated member of the swarm might easily have had the direction of its motion greatly changed, either by the gravitational pull of the other members or by collision with them, so that a single such mass might be seen to enter our atmosphere from an unexpected direction.*

It is therefore in my judgment not impossible that this most interesting fall might have come from the Perseid swarm, and therefore be an actual part of or an attendant to Tuttle's Comet of 1862; but I do not think that from the data at hand we can now establish this connection.

There are several other less striking showers due at about this time; notably, a second Perseid shower of faint, swiftly moving stars whose radiant is 14 degrees farther toward the south than that of the first, and also a shower coming from the constellation

*That the observers' accounts of momentary phenomena often conflict, is but natural. One witness wrote on October 18th, that on hearing the reports, he saw only a very large cloud of sand or smoke move from east to southwest, and after striking a black cloud, the first sand or smoke cloud traveled back to the east. While probably of little value, the account is recorded here because this large finder was the only one to fully indicate an ellipsoid with longest diameter east and west, in answering as to the area of the fall.

of Cygnus, which actually reaches its maximum on this very date,—July 19. But as Cygnus at the time indicated was in the northeastern part of the sky, it seems that this shower must be excluded from consideration for the same reason that the Aquarid shower was dismissed. . . . —*Eric Doolittle.*

Quantitative Comparison.

A most careful search by over one hundred persons was made under that stimulus which is usually found to be instantly effective. This search continued for two months. The discoveries of new stones rapidly rose and as rapidly dwindled to nothing. Following is an estimate of the entire fall. Among the 29 larger ones, three or four had an end broken off, presumably by the finder; perhaps 5 per cent of the stones, counted as complete, had one face merely smoked, the balance were completely incrustated.

Items 1, 2, 3, and 4 were received at Philadelphia.

(1)	29 individuals over 1000 grams : 6665, 4264, 3470, 3122, 2940, 2605, 2520, 2500, 2480, 2463, 2442, 2318, 2270, 2250, 2050, 1893, 1860, 1816, 1780, 1558, 1464, 1400, 1330, 1272, 1190, 1148, 1120, 1100, 1020. Total, 64,810 grams	
(2)	6000 individuals of 1 gram to 1000 grams each.....	136,000 “
(3)	8000 individuals under 1 gram each.....	4,000 “
(4)	Fragments broken after finding (estimated)	4,000 “
(5)	Many individuals of less than 1000 grams each, distributed as samples to institutions in July and carried off as curios by visitors	10,000 “
	14,029 + stones. Estimated total weight of fall (481½ lbs. avd.)	218,810 “

A record of the more notable stone showers of the 19th century was prepared for comparison. It will be observed that such showers are recorded but rarely, and that in point of number of stones, the Holbrook fall is one of the greatest in modern times. Another distinction it carries is the minute size of thousands of its individuals. The smallest shown in fig. 2 average 10,000 to the kilogram, or about 4,536 to a pound avoirdupois: a single one weighs less than 0.1 gram or 1½ grains, being smaller than the smallest of the Hessle stones, which were only found because they fell on the ice.

These scarred and diminutive “Holbrook peas” confirm the accepted opinion that far larger cosmic stones are usually quite consumed in the atmospheric passage.

Principal Stone Showers of the 19th Century.

The following data are gathered from Wülfing's "Meteori-ten":

Date of Fall	Locality	Recorded Number of Stones	Recorded Weight of Fall in Grams
April 26, 1803	L'Aigle, France	2000-3000	36,843
Dec. 14, 1807	Weston, Connecticut	Many	18,267
May 22, 1808	Stannern, Austria	200-300	38,408
May 1, 1860	New Concord, Ohio	Over 30	97,811
June 9, 1866	Knyahinya, Hungary	Over 1000	423,120
Jan. 30, 1868	Pultusk, Poland	About 100,000	200,932
Jan. 1, 1869	Hessle, Sweden	Many	22,895
Feb. 12, 1875	Homestead, Iowa	Many	124,492
Feb. 3, 1882	Möcs, Hungary	Over 100,000	155,632
May 2, 1890	Forest, Iowa	Many	122,037
July 19, 1912	Holbrook, Arizona	Over 14,000	218,310

No other aërolites are recorded from Arizona, the nearest meteoric fall being the siderite of Canyon Diablo, some sixty miles distant.

Philadelphia, October 7, 1912.

NOTE, *Oct. 24th*.—Of the numerous witnesses to whom a list of nineteen questions was submitted, but few replied to the following: In the area covered by the fall, were the large and small stones mixed indiscriminately or were they sorted somewhat according to size? The first answered that the stones were mixed. But in a supplementary statement, Mr. Von Aachen writes on Oct. 18th that he found the small and large stones *separated*. Further evidence is manifestly needed before the actual facts are established concerning a sorting of the shower.

ART. XL.—*Restoration of Limnoscelis, a Cotylosaur Reptile from New Mexico; by S. W. WILLISTON.*

A DESCRIPTION of the skeletal structure of *Limnoscelis paludis* Will., based upon two specimens in the Yale Museum, has been given by me in the papers cited below.*

Since the time of my studies of these specimens they have been thoroughly and carefully divested of their concealing matrix without destroying the relations of the different parts. An additional specimen of the same collections, consisting of pelvis, femora and tail, has also been detected and prepared. A fourth specimen of the same form, of somewhat smaller size, but in excellent condition so far as it goes, collected by myself in New Mexico, has also been of service. From a careful study of all this material, as now prepared, I am able to determine some additional facts in the osteology of this remarkable reptile, and to make a few corrections of my previous papers.

In the restoration given herewith (fig. 32, p. 467), the skeleton as far as the base of the tail has been drawn almost exclusively from the more perfect holotype specimen (No. 811, Yale University). As has been stated, the relations of the bones of this specimen had been disturbed but little in fossilization, except for a part of the tail. Of the tail, the parts preserved are the proximal vertebræ in position, but with the spines somewhat injured; and a nearly continuous series of twenty distal vertebræ. Of specimen No. 809, Yale University, the skull is missing, but the hind feet are in better preservation than those of the holotype; of the tail, twenty-three vertebræ are preserved in articulation with the sacrum, and eighteen distal ones are preserved in several series. Specimen No. 819 (Y. U.) comprises a fragmentary pelvis and incomplete femora, together with the nearly complete tail in natural articulation in the matrix, as shown in figs. 24-26. The caudal vertebræ are in two series; the first, beginning with the fourth (fig. 25), extends to the thirty-third; the second (fig. 25) comprises twelve vertebræ, with which several terminal ones were found associated in the matrix, but separated. Between the first and second of these series, the size indicates a loss of three or four vertebræ, as indicated by the uniform shading of the restoration. From the tip of the tail at least eight or ten are missing, making a total of about sixty, of which forty-eight are actually present in specimen 819,

* This Journal, xxxi, 380, May 1911; American Permian Vertebrates, p. 28, Oct. 1911.

forty-one in specimen 809, and twenty-six in specimen 811. Specimen No. 650 of the Chicago University collections comprises about twenty caudal vertebræ, for the most part connected in a basal series. Unfortunately in none of these specimens are the spines quite complete throughout. From a comparison of the four different specimens, however, most of these have been determined with certainty, as shown in the drawing. In specimen 809 three of the proximal chevrons are preserved complete in natural articulation; in specimen 811 a number of the distal ones are also connected with the centra; while those present in 819 are shown in fig. 25. The three specimens of the Yale collection are almost identical in size, 819 being perhaps a trifle larger than the others, though not much, the total length of the first twenty-three caudal vertebræ being about three-fourths of an inch greater than that of the same vertebræ of 809. The Chicago specimen, however, is distinctly smaller, and also presents some slight differences which might perhaps be accounted of specific value did we know what specific characters are in these old reptiles.

I give herewith a number of figures of some of the best preserved parts of these different specimens, all one-half natural size. The humeri (figs. 1, 2, 31) are best preserved in the Chicago specimen; in the Yale specimen No. 811, from which my previous figure and descriptions were made, the ectocondyle had evidently been crushed somewhat inward from its normal position; it really projects nearly at right angles dorsad from the distal plane of the bone, much as in *Diadectes* and *Diasparactus*. The ectepicondyle is larger and better preserved than in any of the Yale specimens of this bone, and all the processes are better defined. Perhaps the clay matrix has had something to do with the better preservation of this specimen. The radius of the Chicago specimen (figs. 4, 5) in comparison with that of 811, Y. U. (fig. 28), seems to be a little less stout. A well preserved femur and the fibulæ of the Chicago specimen are shown in figs. 6–9, the lower end of the femur completed from that of the opposite side. Especially characteristic of *Limnoscelis*, in which it agrees with *Seymouria*, but disagrees with the *Diadectidæ*, are the large size and low position of the trochanter, and the high, thin adductor crest, as in most of the contemporary amphibians. Both the tibia and the fibula of this specimen are a little less stout, and less expanded at their ends than in the holotype. Two views of a typical posterior dorsal vertebra of this specimen are shown in figs. 15, 16. In my original description of the genus I gave as a characteristic the presence of an infracentral fossa on the presacral vertebræ. I am now not sure whether this character is of importance, since it seems to be absent in the

Chicago specimen, and not well marked in specimen 809 of the Yale collections.

In my original description I gave the probable number of presacral vertebræ in *Limnoscelis* as twenty-five. As a fact

FIGS. 1-5.

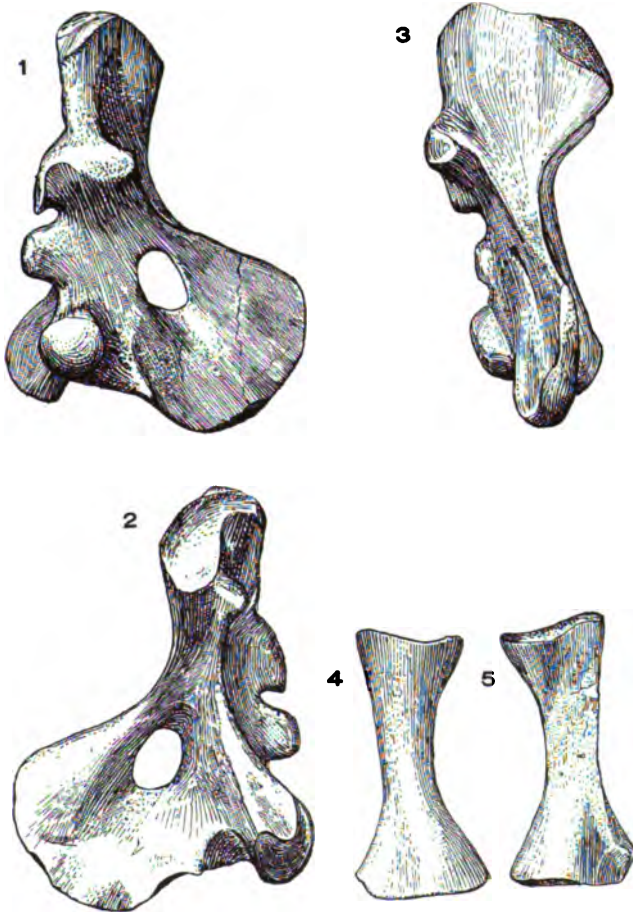


Fig. 1, right humerus, ventral side. C. U. 650. Fig. 2, the same, dorsal side. Fig. 3, the same, ulnar side. Fig. 4, right radius, dorsal side, C. U. Fig. 5, the same, ventral side.

there are twenty-six, a larger number than is known in any other American *Cotylosaur*. All these vertebræ are in intimate matrical contact in the holotype, so that the number is

absolutely fixed. There is not a very great difference between the anterior and posterior ones. The former are a trifle smaller, the spines a very little shorter and less stout, and the diapophyses are longer, those of the notarial vertebræ (as I designate those vertebræ which support the pectoral girdle),

FIG. 6-9.

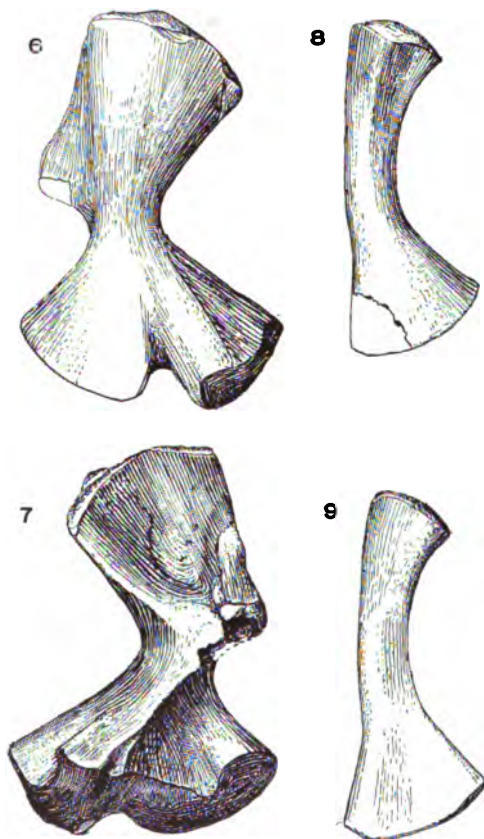


Fig. 6, left femur, dorsal side, C. U. 650. Fig. 7, the same, ventral side. Fig. 8, left fibula, ventral side, C. U. Fig. 9, right fibula, dorsal side, C. U.

as shown in fig. 10, projecting far beyond the zygapophyses, while posteriorly, as shown in fig. 15, they are almost sessile. I have also stated that there is but a single sacral vertebra in *Limnoscelis*, and functionally the statement is true. Strictly speaking, however, the ribs of the vertebra immediately suc-

ceeding the true sacral vertebra touch the ilium at their tip and must, therefore, be considered as sacral ribs. In specimen

FIGS. 10-14.

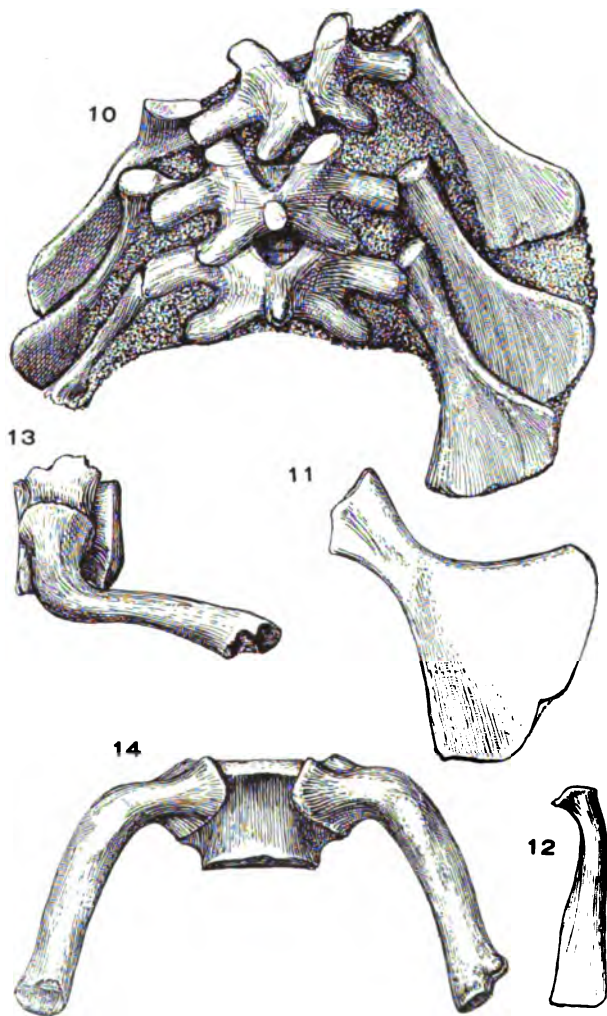


Fig. 10, fourth, fifth and sixth vertebræ. with ribs, as lying in matrix, from above, Y. U. 811. Fig. 11, right sixth rib of same, inner side. Fig. 12, chevron of eleventh caudal vertebra, Y. U. 809. Fig. 13, second caudal vertebra, from the side, Y. U. 819. Fig. 14, the same, from below.

811, the one cleaned at the time of my previous studies, these ribs had been dislodged, but in specimen 809, which has

been since prepared, they are in position. They are about thirty millimeters in length, tapering from the broad proximal end, and again very slightly expanded at the tip, where they touch the ilium immediately above the ilio-ischiadic notch, and just back of the margin of the functional sacral rib. The structure here seems to be quite as in *Diasparactus* and perhaps as in *Diadectes*.

On the basal caudal vertebræ the spines are elongated, as shown in figs. 24 and 25. They decrease very rapidly in

FIGS. 15-23.

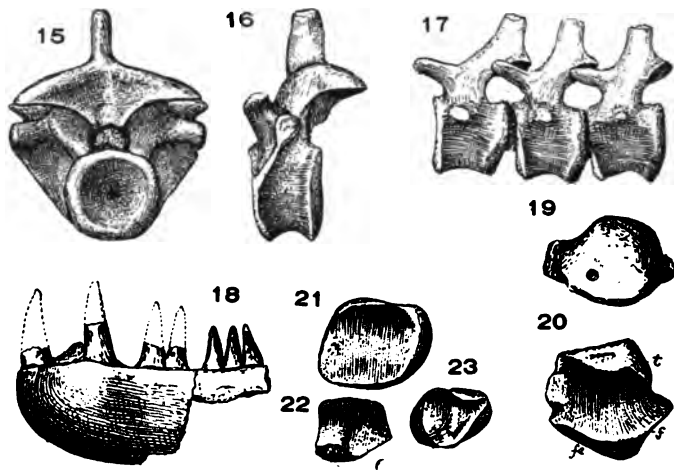


Fig. 15, posterior dorsal vertebra, from behind, C. U. Fig. 16, the same, from the side. Fig. 17, tenth, eleventh and twelfth caudal vertebræ, from the side, C. U. Fig. 18, front end of left mandible, from without, C. U. Fig. 19, astragalus, tibial surface, C. U. Fig. 20, the same, posterior surface. Fig. 21, calcaneum, C. U. Figs. 22, 23, distal tarsals, C. U.

length from the fourth, their height in the eleventh or twelfth (fig. 17), being less than that of its centrum.

The atlas, which lies in specimen 811 nearly above the front margin of the interclavicle, has a large intercentrum which bears an arch on each side. The arch is not unlike that of *Ophiacodon*; it bears a rib on each side on the backwardly directed process. The presence of a proatlas cannot be determined. The odontoid is only in part visible. The axis has a stout and rather broad spine, thickened behind.

Ribs are present on all the vertebræ as far back as the eleventh or twelfth caudal, those of the sacral and caudal regions suturally united with body and arch. They are all holoceph-

alons, the articulation continuous from head to tubercle, unless those of the atlas and axis are exceptions. The axis has a short rib, forty-two millimeters in length, with a width of eighteen at the extremity. The third rib is about sixty-five millimeters in length, and has a distal width of forty. The fourth is seventy-five millimeters in length, with a distal width of about sixty. It is this rib which was figured by me in my cited work, page 36 and plate xxxviii, as a probable hyoid. The fifth rib is scarcely longer than the preceding one, but is broader at the extremity, and the sixth rib, of the same length, is even more expanded at the extremity (fig. 11). These ribs are all thin at the distal extremity and somewhat concave on the inner side. In specimen 811 (fig. 10) the vertebræ lie in position over the pectoral girdle. In settling down, after decomposition of the body had begun, these broad-ended ribs were dragged upward, especially on the right side; all four, that is of the third, fourth, fifth and sixth vertebræ, lie on the inner side of the scapula; the rib of the axis on the left side just underlaps the margin of the scapula. It is very evident that the function of these peculiarly expanded ribs was for the attachment and support of the scapula; in other words, they served the same purpose for the pectoral girdle that the sacral ribs did for the pelvic, and it is evident that their union was nearly or quite as firm. They may properly be called notarial ribs, and their supporting vertebræ notarial vertebræ. These dilated and shortened ribs are more or less characteristic of all American Cotylosauria, and, in a less degree, of *Ophiacodon*, an American pelycosaur.

The seventh rib has nearly the full length of those succeeding, but is unusually stout and broad, especially distally. The following ribs are more slender; they all lie in position in the holotype, and their relative lengths, with the necessary foreshortening, I have endeavored to show faithfully in the restoration. The length of the seventh rib, measured on its chord, is five and three-fourths inches; of the eighth and ninth, six inches; of the fifteenth, five and three-fourths inches; of the eighteenth, three and one-half inches.

The single pair of functional sacral ribs are of the usual diaiectid type, flattened and expanded distally and directed downward, lying in apposition, but not suturedly united, with the inner side of the ilium above the acetabulum. The ribs of the second sacral, or sacrocaudal, vertebra are much less stout than the following ones. The first true caudal ribs are elongate, curved outward and backward, lying inside the posterior prolongation of the ilium for the most part; they terminate apparently in a pointed extremity. The second pair of ribs are extraordinary. In specimen 819, where they are preserved

FIGS. 24-26.

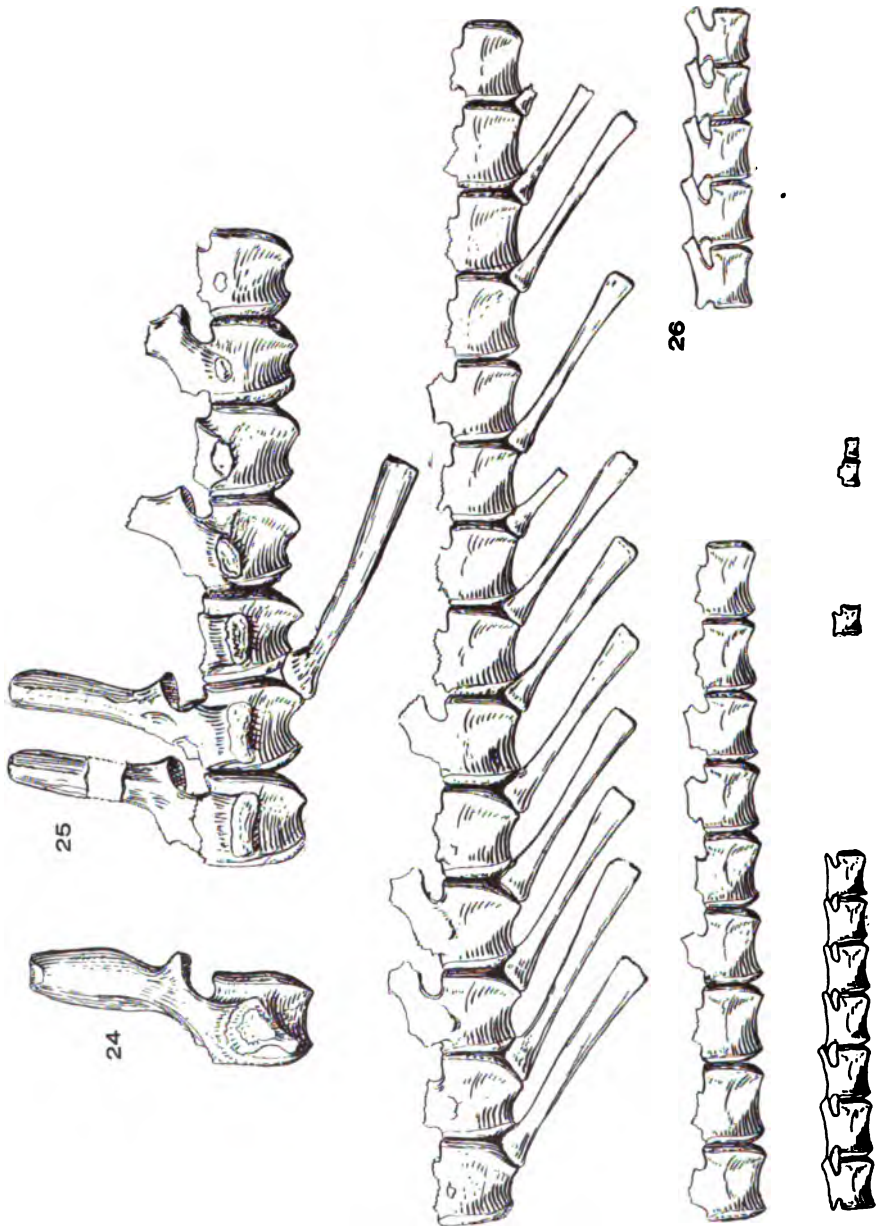


Fig. 24, first caudal vertebra, Y. U. 819. Fig. 25, fourth caudal vertebra and connected series. Fig. 26, second series, Y. U. 819.

complete and undistorted, as shown in figs. 13 and 14, they are remarkably stout and long. They are directed outward, downward, and backward, and end in a truncated extremity. They lie, for the most part, below and back of the iliac process. It seems certain that ribs of such structure and strength in this position must have served some functional use in the support of muscles, doubtless for ones controlling movements of the

FIGS. 27-31.

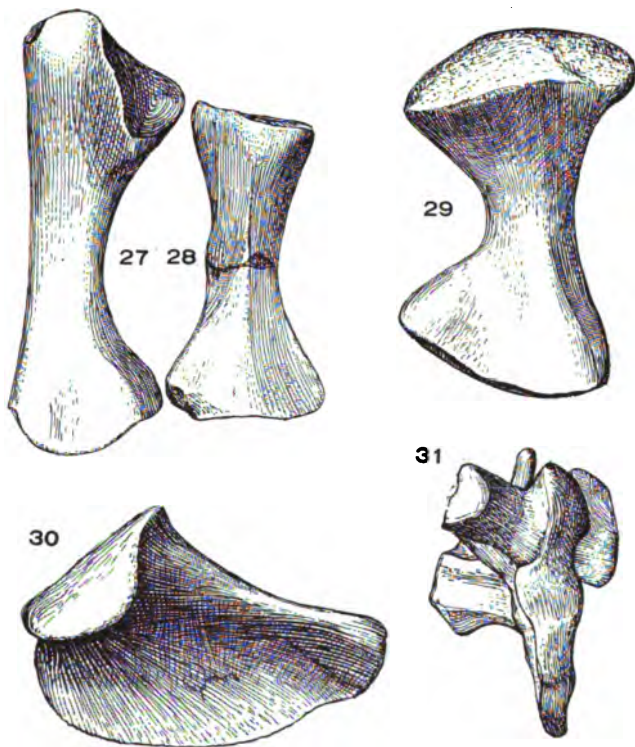


Fig. 27, 28, ulna and radius, dorsal sides, Y. U. 811. Fig. 29, right tibia, ventral side, Y. U. 811. Fig. 30, left ischium, outer side, Y. U. 809. Fig. 31, right humerus, distal end, C. U. 650.

leg. Back of these greatly enlarged and long ribs, the suturally united caudal ribs progressively decrease in length and size, disappearing on the eleventh or twelfth.

In my first paper I stated that the first chevron was attached to the third caudal vertebra; this statement is true if the second vertebra with sacral rib attachments is considered a sacral, not otherwise. The first chevron preserved in specimen 809 is

attached to the under side of the fifth vertebra back of the functional sacral, articulating with the fourth. It is long and slender. Back of this the chevrons are more or less dilated distally and are long; on the distal part of the tail they are more slender.

Large intercentra occur between the anterior caudal vertebrae; one, that articulating between the second and third true caudals, has two small processes on the under side, corresponding to the branches of the chevrons; and all the following chevrons have the proximal end in the form of an intercentrum; another bit of evidence, if such be needed, that the chevrons are merely outgrowths of the intercentra.

As regards the structure of the legs of *Limnoscelis* I have little to add. With one of the feet of specimen 809 Yale University, two small bones are preserved attached to the calcaneum. They are evidently either the third and fourth distalia, or the centrale and a distale, probably the former. In the Chicago University specimen all these four bones are preserved of one foot; I have figured them (figs. 19-23). The astragalus differs distinctly from that of the *Diadectidæ* in its smaller size, and more cuboidal shape. Since the discovery of these small tarsal bones in *Limnoscelis*, it would seem not at all improbable that additional nodules corresponding to the first three distalia, as in *Diasparactus*, may yet be found.

Nor have I much to add regarding the structure of the skull at the present time. I feel confident that I recognize both the tabulare and supratemporal, giving the full complement of cranial elements, with the exception of the intertemporal, known only in *Seymouria*. I give a figure of the anterior end of the Chicago mandible (fig. 18), showing elongate teeth corresponding to those of the premaxillæ. The teeth are implanted deeply in sockets, as in *Diadectes*, and show a deeply infolded dentinal structure.

The characters of *Limnoscelis* may be given as follows, omitting all those common to the *Cotylosauria* of America, as I have recently summarized them: * *Limnoscelis*—Crawling, littoral or subaquatic reptiles, with a rather long body and long tail; probably bare-skinned. Head elongate, narrowed anteriorly, broad behind, with elongate premaxillary teeth, a single row of conical teeth in maxillæ and dentaries; prefrontal and postfrontal meeting broadly over orbits; pineal foramen small; tabularia and quadratojugals present, probably also supratemporals; occipital condyle flattened; basiptyergoid process loosely articulated with pterygoids. Twenty-six presacral vertebrae, their spines short and not rugose at extremity; a single functional sacral vertebra, one sacrocaudal and fifty-five or

* Journal of Morphology, 1912.

more caudals. Ribs holocephalous; notarial ribs of the third to sixth vertebræ greatly expanded for support of pectoral girdle; seventh rib elongated, but stout; ribs continuous to eleventh or twelfth caudal. No ventral ribs. A vestigial cleithrum. Humerus with stout ectocondyle directed dorsad; a well-developed ectepicondyle; entepicondylar foramen large; ulna with olecranon; four bones in proximal row of carpus, and at least three in distal; ungual phalanges short and broad; femur with prominent trochanter near its middle, the adductor crest high; astragalus cuboid in shape, relatively small, as also the calcaneum; at least two bones in distal row of tarsus; phalanges as in front foot. Both front and hind legs short and stout. Length, seven feet. Horizon, Permocarboniferous of El Cobre, New Mexico.

As regards the habits of *Limnoscelis* I have little to add to what I have already written. The very long tail has short spines, except at the base, but the chevrons are longer and stouter than I had expected to find them; and they are, for the most part, more or less flattened at their extremities. The tail must have been somewhat flattened, though by no means compressed as in the crocodiles, unless it bore a carina of horny scutes above. Taking into consideration the very short and stout legs with their broad, flattened feet, the absence of claws, the elongate body and tail, it would seem not at all improbable that *Limnoscelis* was more or less at home in the water, though not strictly an aquatic animal. In much probability it lived in and about the marshes on the mud flats, hiding in dense vegetation, and often taking to the water for protection from its enemies, of which



Fig. 32. Restoration of *Limnoscelis patulidis* Williston, one-eleventh natural size (doubtful parts are shown in uniform shading).

Sphenacodon may have been one, or in seeking its food. The teeth and skull remind one much of *Labidosauros* with its long prehensile teeth in the premaxillæ and front end of the mandibles, teeth well adapted for the seizure and retention of soft and slippery invertebrates, for which it may have probed in the mud. That *Limnoscelis* was piscivorous in habit seems quite improbable. It must have been slow in locomotion, whether on land or in the water, and its prey must also have been slow-moving or stationary. That the creature could have been really burrowing in habit seems out of the question; with its short front legs it could not possibly have excavated burrows for the head to enter.

The length of the skeleton as restored is just seventy-eight inches, a few inches less than I had estimated it to be. It is possible, however, even probable that in my restoration I have not made allowance for the interarticular cartilages, and that the creature was somewhat longer in life, perhaps fully seven feet.

It is a remarkable fact that, so far, not a trace of *Limnoscelis* has been discovered elsewhere than the El Cobre cañon, New Mexico; nothing that can at present be referred to the genus is known from the Puerco or its tributaries. Of the four known specimens, two are said to have come from low down in the cañon, but the specimen collected by myself was found near the top of the fossiliferous horizons, at least two hundred feet above the lowermost beds; it is possible that this difference in their horizons may account for the minor differences presented by this specimen. It is also a little strange that, so far, no specimen of *Sphenacodon* or *Ophiacodon* has been found in the El Cobre cañon. It was in this cañon that Professor Case found a specimen of *Spirifer rockymontanus*, a real Carboniferous fossil, coming probably from an horizon above that of the type of this genus. From all of which it would seem probable that *Limnoscelis* really lived during Carboniferous times.

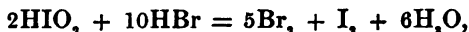
University of Chicago, Chicago, Ill.

ART. XLI.—*The Iodic Acid Process for the Determination of Bromine in Halogen Salts*; by F. A. GOOCH and P. L. BLUMENTHAL.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxvi.]

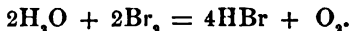
THE oxidation potential of a solution of chlorine in potassium chloride and water is, according to Bancroft,* about 0.241 volt higher than that of a solution of bromine in potassium bromide and water. Iodic acid has an oxidation potential 0.064 volt higher than that of an equivalent and equally acidified bromine solution. The consideration of these oxidation potentials suggested to Bugarsky† the choice of iodic acid as an oxidizer for the liberation of bromine from mixtures containing a bromide and a chloride.

Bugarsky's method of separating the bromine from such a mixture consists in adding sulphuric acid with a known amount of potassium diiodate, and boiling. The bromine and the iodine which are liberated in the interaction of the free acids, according to the equation



escape from the solution and may be collected in the distillate. These free halogens may be made the measure of the bromide taken, or the amount of the bromide may be calculated from the amount of the iodic acid remaining. When the liberated halogens are absorbed in potassium iodide, the amount of free iodine, as determined by titration, proves to be much less than is to be expected from the equation above, and Bugarsky, convinced that the results are much more nearly in accord with the theory when the excess of the iodic acid remaining is made the measure of the reaction, prefers, therefore, to estimate the bromide by determining in an aliquot portion of the boiled solution the iodate which remains, and to determine the chloride in another aliquot portion of the solution by Volhard's process of titration with standard sulphocyanate.

The difference in the results of these two methods of determination Bugarsky attributes to loss of free bromine by the action of steam, in consequence of which hydrobromic acid is formed and oxygen set free, as in the equation



But Andrews points out that hydrobromic acid thus formed, if returned with the condensed steam to the liquid, must be reox-

*Zeitschr. phys. Chem., x, 405.

†Zeitschr. anorg. Chem., x, 387.

idized by more iodic acid, with the result that the bromine determination by calculation from the amount of iodic acid remaining will be high rather than low. Andrews' results for bromine were high to the extent of 1 per cent to 1.5 per cent. The differences in experience and view of these investigators have led us to further investigation of the reaction.

Suitable solutions of sodium chloride and potassium bromide* were prepared and standardized gravimetrically by silver precipitation. An iodine solution, approximately N/10, standardized against N/10 arsenite, and N/10 sodium thiosulphate, standardized against the iodine solution, were used. Finally, a solution of potassium iodate† (3.5670 grams per liter) was prepared, and its iodine value was determined by titrating with the thiosulphate the iodine liberated from 50^{cm} portions by the action of potassium iodide in presence of sulphuric acid. To avoid errors of titration due to an indefinite end point, the gravimetric determination of chlorine was substituted for the Volhard process. Gaseous nitrogen trioxide, liberated from sodium nitrite and washed by nitric acid, was used instead of the sodium nitrite or potassium nitrite used by Bugarsky.

The method of carrying out determinations was as follows: To 50^{cm} of the solution, containing known amounts of sodium chloride and potassium bromide, 50^{cm} of the iodide solution of known value and 10^{cm} of 20 per cent sulphuric acid were added and the solution was diluted to 200^{cm}, in a 500^{cm} Erlenmeyer flask. A few bits of platinum foil were added, to prevent bumping, and the solution was boiled down to about 80^{cm}, some 30 minutes being required. After cooling, the solution was transferred to a carefully calibrated 100^{cm} flask and made up to the mark.

Half the solution was pipetted into an Erlenmeyer flask fitted with an inverted mushroom trap, through which potassium iodide was added. The liberated iodine was titrated with thiosulphate, and 1/6 of it was taken as the equivalent of the excess iodate in the portion.

The remaining half of the solution was transferred to a beaker, the flask and stopper being carefully rinsed, and an excess of gaseous sulphur dioxide (vaporized from the liquid) was passed in. Gaseous nitrogen trioxide (liberated from sodium nitrite or potassium nitrite by nitric acid, and washed by the same) was passed into the solution to destroy the excess of sulphur dioxide acid and to liberate the iodine.‡ The solution was boiled until free from iodine, and the chlorine of the resid-

* The "analyzed" C. P. article, free from chloride, so far as could be determined by qualitative tests, (this Journal (3), xl, 289).

† KIO₃.

‡ The nitrogen trioxide prepared in the manner described produced no turbidity in a solution of silver nitrate acidulated with nitric acid.

nal chloride was precipitated by silver nitrate. After standing over night, the silver chloride was filtered off on asbestos in a perforated crucible, dried at gentle heat, and weighed.

The amounts of potassium bromide calculated from the iodate used up, and the amounts of sodium chloride equivalent to the silver chloride weighed, are given in the table, in comparison with the amounts taken of these substances respectively.

Molecular Ratio of KBr to NaCl, 1:1.

KBr taken. grm.	NaCl taken. grm.	KBr. formed. grm.	NaCl formed. grm.	Error in KBr. grm.	Error in NaCl. grm.	Final volume. cm ³ .
0.1984	0.0974	0.2006	0.0995	+0.0022	+0.0021	*
0.1984	0.0974	0.1981	0.0993	-0.0003	+0.0022	*
0.1984	0.0974	0.1996	0.1003	+0.0012	+0.0029	*
0.1984	0.0974	0.1983	0.0996	-0.0001	+0.0022	*
0.1984	0.0974	0.1939	0.1004	-0.0045	+0.0030	76
0.1984	0.0974	0.1966	0.1008	-0.0018	+0.0034	74
0.1984	0.0974	0.1990	0.0998	+0.0006	+0.0024	38
0.1984	0.0974	1.1945	0.1004	-0.0039	-0.0030	74

* The final volume, 50^{cm} to 75^{cm}, was not measured exactly.

Molecular Ratio of KBr to NaCl, 2:1.

0.1984	0.0487	0.1940	0.0517	-0.0044	+0.0030	50
0.1984	0.0487	0.1904	-----	-0.0080	-----	65
0.1984	0.0487	0.1926	0.1519	-0.0058	+0.0032	68
0.1984	0.0487	0.1965	0.0522	-0.0019	+0.0035	65
0.1984	0.0487	0.1942	-----	-0.0042	-----	78
0.1984	0.0487	0.1945	0.0521	-0.0039	+0.0034	80
0.1984	0.0487	0.1949	0.0518	-0.0035	+0.0031	65
0.1984	0.0487	0.1942	0.0526	-0.0042	+0.0039	70
0.1984	0.0487	0.1959	0.0525	-0.0025	+0.0038	76

Molecular Ratio of KBr; NaCl, 1:2.

0.1984	0.1948	0.1964	0.1954	-0.0020	+0.0006	*
0.1984	0.1948	0.1952	0.1990	-0.0032	+0.0042	*
0.1984	0.1948	0.1967	0.1969	-0.0017	+0.0021	*
0.1984	0.1948	0.1978	0.1984	-0.0006	+0.0036	*
0.1984	0.1948	0.1974	0.1980	-0.0010	+0.0032	*
0.1984	0.1948	0.1983	0.1984	-0.0001	+0.0036	*
0.1984	0.1948	0.1988	0.1985	+0.0004	+0.0037	*
0.1984	0.1974	0.1983	0.1028	-0.0001	+0.0054	75
0.1984	0.1974	0.1960	0.1022	+0.0024	+0.0048	70

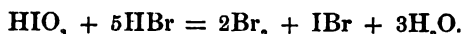
* The final volume, 50^{cm} to 75^{cm}, was not measured exactly.

In these experiments, made with reagents carefully standardized at the outset and restandardized in the course of the investigation, the errors are generally large and irregular, independent of the final concentrations within the limits shown,

and out of all proportion to any possible chloride contamination of the standard bromide. The fact that the chlorine proves to be invariably high and the bromine generally low, suggests the probability that the iodic acid reaction fails to remove all the bromine in the process of boiling.

Bromine was found in the silver chloride obtained from the combined residues of several determinations by applying the chloroform test to the water extract of the sodium carbonate fusion of these residues, after acidulating with sulphuric acid and adding a drop or two of chlorine water. Furthermore, in a special experiment in which pure potassium bromide was treated according to the procedure outlined, the titration figures of the excess of iodate corresponded to only 0.1945 gm. of potassium bromide out of 0.1984 gm. taken; while, after treatment with sulphur dioxide followed by nitrogen trioxide, and boiling until all iodine had been expelled (as shown by the starch test applied to the cool solution), silver nitrate precipitated from the solution silver bromide equivalent to 0.0036 gm. of potassium bromide. The 0.1945 gm. of the potassium bromide indicated by the determination of the iodate and the 0.0036 gm. equivalent to the silver bromide precipitated after reduction make up 0.1981 gm. of the 0.1984 gm. taken. In this experiment, therefore, the deficiency of bromine and the excess of chlorine noted were plainly due to the retention of bromine, after the iodic acid treatment, in some combination such that the process of reducing the residual iodic acid and expelling the iodine left it in condition to be precipitated as silver bromide, which was counted as silver chloride.

The combination of iodine with bromine in this experiment and of iodine with bromine and chlorine in the experiments of the table, would account for the observed deficiencies in bromine and excess in chlorine; and a little consideration shows that the conditions of the process are favorable to the formation of such combinations. Thus free bromine and free iodine, both products of the main reaction, may readily combine to form iodine monobromide,



Furthermore, Roberts* has shown that iodic acid, iodine, and aqueous hydrochloric acid react to form iodine monochloride, according to the reaction



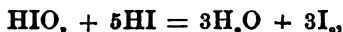
and it may reasonably be expected that in the reaction of iodic acid and hydrobromic acid in presence of free iodine (pro-

* This Journal (3), xlviii, 1, 58.

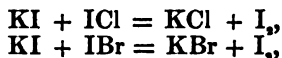
duced in the main reaction, previously cited) iodine monobromide will be similarly formed, according to the equation



When the acidulated solution containing an excess of iodic acid with more or less iodine monochloride, or monobromide, is treated with potassium iodide for the purpose of determining the excess of iodic acid by means of the iodine liberated,



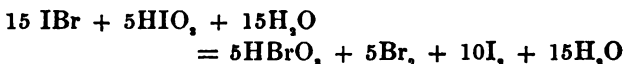
the iodine compounds of the halogens will contribute to the amount of the free iodine which measures the iodic acid,



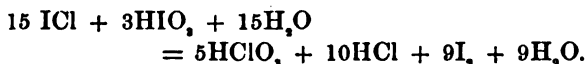
and this increase in free iodine will produce a corresponding deficiency in the bromide, which is estimated from the amount of iodate which has disappeared.

When, on the other hand, the excess of iodate is reduced by sulphur dioxide preparatory to determining the chloride, the iodine monochloride is converted to hydriodic acid and hydrochloric acid, and the iodine monobromide to hydriodic acid and hydrobromic acid. The hydriodic acid is destroyed, and the iodine removed, in the subsequent treatment with nitrogen trioxide; the hydrochloric acid is regularly estimated as silver chloride; but the hydrobromic acid remains to produce silver bromide, which contaminates the silver chloride and causes an error of excess in the chloride determination.

These hypothetical effects are in precise accordance with the observed phenomena. It is conceivable, and even probable, that chloric acid and bromic acid may appear also as products of the hydrolysis of the halogen compounds in presence of water and iodic acid. Thus the hydrolysis of iodine monobromide may proceed according to the expression



and that of iodine monochloride according to the equation



The production of bromic acid by hydrolysis of iodine bromide, with elimination of the free halogens and substitution of bromic acid for an equivalent amount of iodic acid, will tend to reduce the tendency to negative errors in the determination of bromine; but the bromine of the bromic acid will still be

capable of contaminating the silver chloride precipitated by silver nitrate after reduction.

The effect of chloric acid substituted for iodic acid will depend upon the conditions of concentration. So far as it may act as an oxidizer in the treatment of potassium iodide, it will tend to produce a positive error in the determination of bromine. So far as it escapes reduction in the treatment of sulphur dioxide and nitrogen trioxide, it will tend to produce an error of deficiency in the determination of chlorine.

The extent to which these various possibilities may influence results will depend upon the conditions of action and possible balancing of errors. The experimental results given above show plainly that under the conditions defined the separation of bromine from chlorine in halogen salts by the action of iodic acid, though based upon a reaction ideal in respect to the relation of the oxidation potentials, is vitiated by secondary effects. These effects may be reasonably attributed to the action of small amounts of iodine monochloride and iodine monobromide formed in the interaction of iodic acid and free iodine with hydrochloric acid and hydrobromic acid, or to the action of chloric acid and bromic acid derived from iodine monochloride or bromine monochloride by hydrolysis.

ART. XLII.—*A New Chlorite from Northern Wyoming*; by
JOHN E. WOLFF.

IN December, 1910, the writer received from Mr. Albert F. Holden of Cleveland, Ohio, a talc-like mineral which he had in turn received from Mr. W. G. Swart, a mining engineer of Denver, as apparently containing a large amount of alumina. By correspondence with Mr. Swart it was ascertained that the mineral had been brought in by prospectors who were reluctant to disclose the actual place of the find but from whom finally the following information was obtained. To quote Mr. Swart's letter: "Location—Sheridan County, Wyoming. Occurrence—as nearly as I can make out from Mr. Heineman's description, it occurs in a vertical vein. He describes the exposed face as being 'as high as the office ceiling' and about 6 to 8 feet wide. The lines of fracture run vertically in the body of the mineral. This information was obtained by Mr. Parmelee, who originally brought me the mineral."

Sheridan County lies along the northern border of the state, a little east of the center, and includes in its western half the uplift of the Big Horn Mountains, in which the pre-Cambrian crystalline rocks are exposed. In the published reports these are described as mainly granite with some bands of schist, hence the only deductions possible from this scanty information is that the mineral occurs as a vertical schist band six to eight feet wide, representing either a shear zone or an integral member of a series of crystalline schists.

Description of the Mineral.

Macroscopic characters.—Several pieces were received, the largest a slab 7 in. long, 3 wide, and $\frac{1}{4}$ in. thick. The material is well foliated, with fine straight foliation planes like a roofing-slate, has a faint silvery green color and is decidedly translucent even in the thicker pieces, while thin splinters are colorless and almost glassy. The specimen is homogeneous and composed of minute parallel scales of the mineral.

Microscopic characters.—The thin sections confirm the purity of the material, for with the exception of a few minute prisms of zircon (?) and fluid cavities it is composed of sub-parallel plates of the chlorite, sometimes interlocking with a tendency to radial arrangement, with an average thickness across the base of $1/10^{\text{mm}}$ and diameter on the base of $2/10^{\text{mm}}$. No twinning is seen and no crystalline outlines, but a good basal cleavage.

Optical properties.—Dr. H. E. Merwin, of the Geophysical Laboratory, Washington, has kindly made the following measurements, entirely with the microscope:

$$\alpha = 1.580 \quad \beta = 1.580 \text{ to } 1.581 \quad \gamma = 1.589$$

with a possible error of $\pm .001$. 2E measured on several plates

about $1/10^{\text{mm}}$ in diameter varied from 26° to 50° , but the angle of most of the cleavage flakes is about 35° . The acute bisectrix, "Z," is inclined 5° to 10° to c . On account of the indistinctness of the interference figures the dispersion of the optic axes could not be measured satisfactorily.

Chemical composition.—The following analysis (I) was made by the writer, employing the usual methods and determining the water directly by the Penfield method. No reaction was obtained for fluorine. To ascertain any difference in the state of the water given off above 110° the mineral after constant weight at that temperature was heated an hour at 250° to 300° without change and at 350° for half an hour with practically no change, the whole of the water going off at a white heat and hence considered water of constitution.

	I	Mol.	II
SiO ²	= 28.81	477	= 2 32.1
Al ² O ³	= 26.43	259	} = 1 18.5
Fe ² O ³	= 0.24	1.5	
MgO.....	= 31.21	773	} = 3 36.7
FeO.....	= 0.40	5	
H ² O			0.6
+110 ..	= 12.62	700	} = 3 12.1
-110 ..	= 0.09		
Na ² O ..	= 0.35	5	
K ² O	= 0.14	1.5	
CaO.....	None		
	100.29		100.0

I. Chlorite from Wyoming. II. Leuchtenbergite, Mauléon, Delesse, Ann. Chim. and Phys., ix, p. 396, 1843.

Specific gravity (pycnometer) 2.702.

Pyrognostics.—Thin fragments fuse with difficulty in the blowpipe to a snow-white enamel and give intense blue with cobalt solution. Water given off in closed tube is neutral or very slightly alkaline. Slowly decomposed by boiling sulphuric acid and with difficulty by hydrochloric.

Conclusion.—The simplest empirical formula from the ratios of the above analysis is $\text{H}_2\text{Mg}_2\text{Al}_2\text{Si}_2\text{O}_{12}$. The leuchtenbergite from Mauléon, Pyrenees, of which only the old analysis of Delesse (II above) is available, seems to be the only chlorite containing as little iron, although the composition differs greatly by the excess of alumina in the Wyoming mineral, which amount is in fact exceeded by few chlorites. Although it seems hardly permissible to add a new name to the forty or fifty now found under the chlorite group, yet the purity of this material, its peculiar chemical composition and the certainty that it will be available in large quantity, perhaps justifies the name of "Sheridanite," from the county in which it occurs.

SCIENTIFIC INTELLIGENCE.

I. CHEMISTRY AND PHYSICS.

1. *The Dissociation of Hydrogen into Atoms.*—It has been found by IRVING LANGMUIR that at extremely high temperatures the power consumption necessary to maintain a tungsten wire at a given temperature in hydrogen gas increases with abnormal rapidity with the temperature. This rapid increase in loss of heat could not be explained by simple convection or conduction, and the most probable explanation appeared to be that dissociation of the hydrogen molecules (H_2) into atoms was taking place. This dissociation in the region close to the hot wire would absorb large quantities of energy, the hydrogen atoms would then diffuse out into the gas at some distance from the wire and would then recombine and give out the heat of the reaction, thus causing an abnormally high heat conductivity. This view is strengthened by the fact that Magnanini and Malagnini have observed that the heat conductivity of nitrogen peroxide is three times as great with the partly dissociated gas as when it is completely dissociated. Langmuir has made this explanation still more probable by calculating the energy loss from heated wires by means of simple equations and finding that the calculations agree well with the experimental results in the cases of nitrogen gas and mercury vapor up to 2500° C. (abs.), and also in the cases of carbon dioxide and air up to the melting-point of platinum, while in the case of hydrogen there is agreement only up to about 2100° C. (abs.), and above that point the energy loss increases very rapidly until at 3300° it is four or five times as great as the calculated value. It was shown by experiments that the phenomenon is an actual dissociation which follows the law of mass action, and that the volume of the dissociation products is approximately twice the volume of the original hydrogen, as the equation $H_2 = 2H$ requires. The heat of this reaction was found to be 550,000 joules, or 130,000 calories at constant volume. The extent of the dissociation at atmospheric pressure was calculated to be such that the partial pressure of the atomic hydrogen at 3300° C. (abs.) is two-thirds of the total pressure.—*Jour. Amer. Chem. Soc.*, xxxiv, 860. H. L. W.

2. *The Determination of Sulphur in Pyrites.*—This important determination has given much trouble to analytical chemists in the past, and it has been the subject of many investigations. ALLEN and BISHOP have now devised and have carefully tested a new method for this purpose, which gives constant and accurate results, and which promises to supersede the older methods. The main features of the process consist in decomposing the substance with a mixture of liquid bromine and carbon tetrachloride with subsequent addition of strong nitric acid, the

evaporation of these reagents, the conversion into chlorides and the separation of silica by evaporation with hydrochloric acid, drying, and dissolving in the same acid, the reduction of ferric chloride to ferrous chloride by the addition of aluminium powder, the precipitation of barium sulphate by the slow addition of dilute barium chloride to the cold liquid, which is diluted very largely and is not stirred during the addition of the reagent, and finally the weighing of the barium sulphate in a Gooch crucible. It was found that iron in the ferrous condition does not interfere with the precipitation, and that although a little barium chloride is occluded in the precipitate this error appears to be compensated by solubility, so that it is not necessary to make any correction in the results.—*Proceedings 8th Internat. Congress App. Chem.*, i, 33. H. L. W.

3. *Separation of Arsenic from Antimony and other Metals.*—MOSER and PERJOTEL have devised a convenient method for removing arsenic from other metals by distilling it off with a current of air at the temperature of the water bath from a strong hydrochloric acid solution containing methyl alcohol. If the arsenic is in the higher state of oxidation, a reducing agent, preferably a ferrous salt, must also be added. The arsenic goes over partly as trichloride and partly as methyl arsenite, both of which are decomposed by water in a receiver, into which the air and vapors are passed. The chief advantages of the method consist in the avoidance of a stream of hydrochloric acid gas, and the rapidity and completeness of the separation. Only about 1½ hours are required for the distillation. The test analyses given are very satisfactory.—*Monatshefte*, xxxiii, 797. H. L. W.

4. *Methods in Chemical Analysis*; by FRANK AUSTIN GOOCH. 8vo, pp. 536. New York, 1912 (John Wiley & Sons).—Analytical chemists everywhere will welcome this summary by Professor Gooch of the methods worked out by himself and his pupils in the Kent Chemical Laboratory of Yale University, and published in this Journal during the past twenty-two years. The book in giving this condensed account of these researches is very impressive in showing not only the great number of the investigations, but also their high quality and importance. Professor Gooch is to be most highly congratulated for what he has done for the benefit of analytical chemistry, and it is to be hoped that his valuable work will continue for many years to come. H. L. W.

5. *Elementary Applied Chemistry*; by LEWIS B. ALLYN. 12mo, pp. 127. Boston, 1912 (Ginn and Company).—At a first glance this book has a somewhat humorous aspect. The frontispiece is a photograph of a large class of young ladies working in a laboratory where the results of ice-cream analyses are displayed upon a blackboard, and also in the preliminary "Suggestions to Teacher and Pupil" the heating together of aniline, caustic potash solution and chloroform is recommended, "if the odor of

phenyl carbamine is unknown," although it might be feared that the horrible odor of the isonitrile might discourage the beginner. However, upon examining the book more carefully it is evident that it presents a very interesting and useful course of laboratory work. The author says that these experiments and tests have been of personal value to hundreds of earnest students. This can be well believed, as the course deals with many matters of vital importance; for instance, the examination of water, baking powder, milk, ice-cream, cheese, headache-powders, paint and oils, the detection of coal-tar dyes, food preservatives, arsenic, methyl alcohol, the determination of food values, etc. As the title of the book and its size indicate, the topics are treated in an elementary manner, but it seems to be very well adapted for its purpose.

H. L. W.

6. *A Dictionary of Applied Chemistry*; by SIR EDWARD THORPE. Revised and enlarged edition, Vol. II, 8vo, pp. 786. London, 1912 (Longmans, Green and Co.).—The second volume of this important work extends from CHI to GOV. It contains many important articles, and the matter appears to be well brought up to the present state of the science. Among the interesting longer articles are those on chlorine, coke manufacture and the recovery of by-products, disinfectants, dyeing, identification of dyestuffs on fabrics, explosives (73 pages), fermentation, fertilizers, fuel, gas, glass, etc. The volume maintains the high standard of the previous one as a valuable work of reference.

H. L. W.

7. *Die äussere Reibung der Gase und ein neues Prinzip für Luftpumpen: Die Molekularluftpumpe*.—As early as 1875 Kundt and Warburg showed that highly rarefied gases slip along the walls of the containing vessel, and that the superficial friction of the gas decreases with the pressure. In 1909 Knudsen calculated the numerical value of the friction between the inner surface of a glass tube and the stream of gas flowing through the tube, and found good agreement between the experimental and theoretical data. Quite recently W. GAEDE has repeated Knudsen's observations and found that, at pressures greater than 0.001^{mm} of mercury, a film or skin of gas is formed on the glass and that this layer is predisposed to throw back the molecules in the general direction of incidence. Furthermore, Gaede's experiments indicated that the action of the gaseous skin may be fully accounted for in the following manner. Two kinds of unevennesses on the glass wall are to be distinguished, (a) "mechanical" rugosities, and (b) "molecular" inequalities. At pressures above 0.001^{mm} the molecular unevennesses are covered up by a film of gas whose density decreases towards the free interior of the gas. The gas molecules which are reflected from the solid wall must pass through the skin of gas and consequently their direction of emergence will be affected. More specifically, normal passage through the skin is the most favorable because, for oblique reflection, the length of path in the skin is greater and hence oblique emergence is more

difficult. In substance, Gaede says : " If we compare the mechanical rugosities with the hills and furrows of a ploughed field, then the molecular unevennesses correspond to the grains of sand and small stones, and the gaseous skin corresponds to a thin layer of hoarfrost or to a light coating of snow upon the hills." If a difference in gas pressure exists at the ends of a comparatively highly exhausted tube, the processes favorable to equalization of pressure will be hindered by the gaseous skin and the mechanical inequalities. For the molecules which have a component of velocity towards the more remote end of the tube, and which also impinge against the wall, will strike the mechanical inequalities of surface which are turned towards them so that, as stated above, the gaseous skin will, in the majority of cases, send the molecules back along their lines of incidence towards the end of the tube from which they had come. On the other hand, when the degree of exhaustion has been carried so far that no gaseous film remains on the walls, the molecules will be reflected by the molecular unevennesses of the walls in a perfectly regular manner, that is, without any selective relation to the angle of incidence. Therefore, just as many molecules will be thrown back towards one end of the tube as will be sent forward towards the other end. In this case, the equalization of pressure will proceed more rapidly than when a gaseous skin adheres to the tube. At about 0.001^{mm} this film practically vanishes, so that for lower pressures the assumption of regular, non-selective reflection holds and the Kinetic Theory of Gases applies in its more elementary form.

An obvious extension of the preceding considerations to the case of the friction between a gas and a cylinder rotating in the gas has been made by Gæde. The result is that he has designed and tested a pump which bids fair to revolutionize the production of extremely high vacua. It is so difficult and wasteful of space to clearly describe the construction of a piece of apparatus without the aid of diagrams that the attempt will not be made to go into full details here. Suffice it to say that the "Molecular Air-pump" consists essentially of a cylinder which can be revolved at very high speed inside of a coaxial cylinder or housing. The housing is grooved or recessed over a certain arc and in a plane perpendicular to the common axis of the cylinders. The "leading" and "trailing" ends of the recess communicate respectively with the auxiliary pump and with the vessel to be exhausted. In practice, a number of grooves and inlet and outlet tubes are placed in series or tandem. At pressures below 0.001^{mm} the molecules of the gas are diffusively reflected at the metallic surfaces and fly from one wall to the other without, in general, colliding with other molecules of their kind. "The reflection of the molecules can be pictured as if the surface of the cylinder were covered with a great number of small cannon out of which the molecules are shot in all possible directions with a certain speed, the molecular speed." If the surface of the cylinder moves with a linear speed greater than the molecular speed, then the molecules inside the

recess which are shot out tangentially forwards from the cylinder will have a velocity directed away from the trailing or inlet tube and towards the leading or outlet pipe. Their speed will be more than twice the mean molecular speed. Theoretically, an extremely small percentage of molecules can pass in the opposite direction.

From the practical standpoint, as well as from the theoretical, the molecular air-pump is almost perfect. When run at a speed of 12000 R.P.M. the pressures at the "suck-nozzle" were 0.0003, 0.00003, 0.000005, and 0.0000002^{mm} when the pressures in the housing were 20, 10, 1 and 0.05^{mm} respectively. The commercial pumps are designed to run at 8000 R.P.M. A conception of the rapidity of working of the new pump may be formed from the following test. An X-ray tube of about one liter capacity was evacuated, in 10 secs., from about 5^{mm} to a pressure so low that sparks passed in a parallel gap 15^{cm} long. Gaede's well-known mercury pump required 100 secs. to bring about the same result. Another great advantage of the molecular air-pump is that it works just as well for vapors as for dry gases. In particular, therefore, the usual drying agents may be dispensed with and much time saved in this connection. Of course, the new pump alone is useless at atmospheric pressure.—*Physikal. Ztschr.*, No. 18, Sept. 1912, p. 864.

H. S. U.

8. *On the Emission Velocities of Photo-Electrons.*—The results obtained by various investigators in this field have been discordant, and hence the present paper by A. LL. HUGHES is rather important because in it he discusses the sources of error which may have vitiated, in a greater or lesser degree, the work of his predecessors, and also describes his method of experimenting, which seems to overcome most of the difficulties. The two sources of error which have not been taken into account in any previous work are: (a) the effect on the velocity-distribution curves of a magnetic field, such as, for example, that of the earth, and (b) the effect on such curves of an electron approaching the boundary obliquely. By distilling the metal to be investigated and by allowing it to deposit on a disc of nickel, which could be raised and lowered at will inside of the glass apparatus itself, Hughes avoided both the production of surface films of gas and the polarization of the metallic surface which arises when the method of anode sputtering is employed. The whole process of distillation and adjustment was carried out in a liquid air vacuum, so-called. A control experiment was performed by using the surface of flowing mercury in place of the solid metal deposited on the nickel disc.

A portion of the summary given by Hughes will now be quoted. "(1) The maximum velocity of photo-electrons from the surfaces of a number of elements prepared by distillation *in vacuo* has been measured. (2) It has been shown that the energy of the fastest electrons emitted when monochromatic light falls on the surfaces is proportional to the frequency of the light. The

results are expressed in the form $V = kn - V_0$, where V is the velocity measured in volts and n the frequency. LADENBURG's law, that the velocity is proportional to the frequency, has been shown to be incorrect. (3) The values of k and V_0 have been found directly for the elements Ca, Mg, Cd, Zn, Pb, Sb, Bi, and As, and the values of V_0 for Se and O, indirectly. (4) The values of k and V_0 for elements of the same valency change regularly with the atomic volume. (5) The product of V_0 into e , the charge of an electron, has been identified with the work required to separate an electron from the molecule." Conclusion (2) is especially worthy of note.—*Phil. Trans. Roy. Soc., London*, Vol. 212, A, p. 205. H. S. U.

9. *Magnetism and Electricity*; by E. E. BROOKS and A. W. POYSER. Pp. viii, 633; 413 figures and 414 problems. London, 1912 (Longmans, Green & Co.).—This volume has been prepared to replace Poyser's *Advanced Magnetism and Electricity*, which was originally published in 1892. Nearly the whole of the subject-matter has been rewritten on modern lines, so that, for all practical purposes, the only feature of the old book which remains is the experimental form. "The present work is intended to afford such a range of general reading in the subject as is desirable for the majority of students, before they begin to specialize either in pure science or in the various branches of electrical engineering." An elementary knowledge of algebra, geometry, trigonometry, and mechanics is assumed. Nevertheless, in many instances, the authors supplement the more elementary analysis by short, alternative proofs in which the processes of the differential and integral calculus are used. When the elementary demonstrations would lack rigor or would be very cumbersome, the calculus alone is used. The brevity and elegance of the latter proofs should stimulate the student who is not acquainted with this powerful branch of analysis to increase his mathematical attainments. The chapters entitled "Introduction to the Theory of Alternating Currents," "Measurement of Inductance," "Passage of a Discharge through Gases," and "Effect of Inductance and Capacity at Starting and Stopping a Current—Electric Oscillations—Radiation—Wireless Telegraphy and Telephony" are starred to indicate that they may be omitted because of their relatively greater degree of advancement. Of necessity, the proofs in the last of these chapters involve a knowledge of elementary differential equations. The usual symbols K and μ have been retained in the formulæ in order to keep the dimensions of the equations correct.

Throughout the volume, 245 practical exercises are suggested in small print. Many of the qualitative experiments do not require special laboratory apparatus, so that the student can perform them at home with improvised material. The numerical problems and questions are collected in groups at the ends of the chapters, and the answers to the former are given just before the index. Most of the figures are new and all of them are clear-cut

and satisfactory. Our opinion of the book may be best expressed by the statement that we shall use it in one of our intermediate courses during the coming winter.

H. S. U.

10. *A Text-Book of Physics, Third Edition*; edited by A. W. DUFF. Pp. xvi, 886; 595 figures and 284 problems. Philadelphia, 1912 (P. Blakiston's Son & Co.).—A careful comparison of the latest edition of this work with the second (see vol. xxviii, page 556) brought out the following facts. The chapter on heat, which was formerly composed by Guthe, has been entirely rewritten by Mendenhall. In the subjects of electricity and magnetism Goodspeed has surrendered his pen to Carman. The articles on sound and mechanics have not suffered much alteration. Lewis has decreased the number of pages devoted to light from 140 to 118, while McClung has brought the numerical data in the conduction of electricity through gases and in radio-activity up to date. The sequence of subjects has been changed to the following order: (1) mechanics, (2) wave-motion, (3) heat, (4) electricity and magnetism, (5) gaseous conduction and radio-activity, (6) sound, and (7) light. Some of the figures have been replaced by new and clearer diagrams, they all appear to have been relettered, and the total number of figures has been increased by seventy. Four-place tables of the common logarithms of numbers and a table of natural sines and cosines have been introduced immediately before the first index. Great care seems to have been taken to avoid the old typographical errors and to give the text a more polished and elegant appearance.

H. S. U.

11. *Gravitation*; by FRANK HARRIS. Pp. xi, 107; 18 figures. London, 1912 (Longmans, Green & Co.).—Less than six full lines are devoted to the preface, which amounts to the confession that the volume may not be "entirely free from clerical errors" and may "involve erroneous deductions." Furthermore, the introduction deals only with the question of the meaning to be attached to the word "explanation," when dealing with natural phenomena. Hence, the author gives no explicit clue to the object which he had in writing the book or to the gap which the text is intended to fill in the literature of the subject. The text is highly mathematical and the figures are graphs of certain functions. The titles of the chapters are:—I Medium, Particle and Motion; II Spheres in Sequence; III Potential Energy; IV Sources and Sinks; V Two Circles; VI Spheres in Parallel; and VII The Dimensions of Space. The volume closes with a chapter on "Atomic Forces," which is presented as an appendix. On page 29 the author uses the term "veetal" to signify "the loss of potential energy in an attracted particle due to its transfer from infinity to a given point."

H. S. U.

II. GEOLOGY AND MINERALOGY.

1. *Publications of the United States Geological Survey*; GEORGE OTIS SMITH, Director.—Recent publications of the U. S. Geological Survey are noted in the following list (continued from vol. xxxiii, p. 507, May, 1912):

TOPOGRAPHIC ATLAS: Fifty-five sheets.

FOLIO No. 182.—Geologic Atlas of the United States Choptank Folio, Maryland; by B. L. MILLER. Surveyed in coöperation with the State of Maryland. Pp. 8; 2 colored maps, 3 figures.

PROFESSIONAL PAPER No. 77.—Geology and Ore Deposits of the Park City District, Utah; by JOHN M. BOUTWELL, with contributions by LESTER H. WOOLSEY. Pp. 231; 44 plates, 18 figures.

MINERAL RESOURCES of the United States in 1911. Numerous advance chapters.

BULLETINS No. 471.—Contributions to Economic Geology, 1910, Part II. Ten advance chapters.

No. 498. Headwater Regions of Gulkana and Susitna Rivers, Alaska, with accounts of the Valdez Creek and Chistochina Placer Districts; by FRED H. MOFFIT. Pp. 82; 10 plates, 9 figures.

No. 506. Geology and Mineral Resources of the Peoria Quadrangle, Illinois; by J. A. UDDEN. Pp. 103; 9 plates, 16 figures.

No. 507. The Mining Districts of the Western United States; by JAMES M. HILL, with a geologic Introduction by WALDEMAR LINDGREN. Pp. 309; 16 plates, one figure.

No. 509. Mineralogical Notes. Series 2; by WALDEMAR T. SCHALLER. Pp. 115; one plate, 5 figures.

Nos. 514, 516, 517, 519. Results of Spirit Leveling: R. B. MARSHALL, Chief Geographer. No. 514, New York, pp. 139. No. 516, Florida, pp. 24, one plate. No. 517, Alabama, pp. 38. No. 519, Tennessee, pp. 45.

No. 520. Mineral Resources of Alaska. Twelve advance chapters.

No. 530. Contributions to Economic Geology, 1911, Part I, eleven advance chapters.

WATER SUPPLY PAPERS No. 279.—Water Resources of the Penobscot River Basin, Maine; by H. K. BARROWS and C. C. BABB. Prepared in coöperation with the Maine State Survey Commission. Pp. 285; 19 plates, 5 figures.

Nos. 285, 291. Surface Water Supply of the United States, 1910. Prepared under the direction of M. O. LEIGHTON. No. 285. Part V, Hudson Bay and Upper Mississippi River; by ROBERT FOLLANSBEE, A. H. HORTON, and G. C. STEVENS. Pp. 318; 4 plates. No. 291. Part XI, Pacific Coast of California; by W. B. CLAPP, F. F. HENSHAW and H. D. MCGLASHAN. Pp. 218; 4 plates, one figure.

Nos. 295, 296. *Gazetteer of Surface Waters of California*. Prepared under the direction of JOHN C. HOYT by B. D. WOOD. Part I, Sacramento River Basin. Pp. 99. Part II, San Joaquin Basin. Pp. 102.

2. *Publications of the Bureau of Mines*; JOSEPH A. HOLMES, Director.—The First Annual Report of the Director of the Bureau of Mines was noticed on p. 305 of this volume. There are now to be mentioned the numerous publications issued by the Bureau in the past few months (see vol. xxxiii, p. 63). These include the following Bulletins:

No. 6. Coals available for the Manufacture of Illuminating Gas; by A. H. WHITE and PERRY BARKER, compiled and revised by HERBERT M. WILSON. Pp. 77; 4 plates, 12 figures.

No. 10. The Use of Permissible Explosives; by J. J. RUTLEDGE and CLARENCE HALL. Pp. 34; 5 plates, 4 figures.

No. 15. Investigations of Explosives used in Coal Mines; by CLARENCE HALL, W. O. SNELLING, and S. P. HOWELL; with a chapter on the Natural Gas used at Pittsburgh by G. A. BURRELL and an Introduction by CHARLES E. MUNROE. Pp. 197; 7 plates, 5 figures.

No. 16. The Uses of Peat for Fuel and other Purposes; by CHARLES A. DAVIS. Pp. 214; one plate, one figure.

No. 18. The Transmission of Heat into Steam Boilers; by HENRY KREISINGER and WALTER T. RAY. Pp. 180; 78 figures.

No. 23. Steaming Tests of Coals and Related Investigations, September 1, 1904, to December 31, 1908; by L. P. BRECKENRIDGE, HENRY KREISINGER and WALTER T. RAY. Pp. x, 380; 94 figures.

No. 25. Mining Conditions under the City of Scranton, Pa. Report and Maps, by WILLIAM GRIFFITH and ELI T. CONNER. With a preface by JOSEPH A. HOLMES and a chapter by N. H. DARTON. Pp. 89; also 29 maps in separate cover.

No. 41. Government Coal Purchases and Specifications with Analyses for the fiscal year 1909-10; by GEORGE S. POPE, with a chapter on the Fuel-Inspection Laboratory of the Bureau of Mines; by JOSEPH D. DAVIS. Pp. 97; 3 plates.

No. 44. First National Mine-safety Demonstration, Pittsburgh, Pa., October 30 and 31, 1911; by H. M. WILSON and A. H. FAY. Pp. 75; 8 plates, 4 figures.

No. 47. Notes on Mineral Wastes; by C. L. PARSONS. Pp. 44.

Fifteen Technical Papers, many of them of great practical importance particularly as dealing with the conditions in coal mining, have also been issued.

3. *The Onondaga fauna of the Allegheny region*; by E. M. KINDLE. Bull. 508, U. S. Geol. Surv., 144 pages, 13 plates, 1912.—The middle Devonian Onondaga limestone, which is of wide distribution and forms an important datum plane in the eastern portion of North America, is said by many geologists to be absent in the Allegheny region south of Central Pennsylvania. Kindle now shows, after a great deal of detailed work, that the Onondaga is also present in the latter region, but in the main as a calcare-

AM. JOUR. SCI.—FOURTH SERIES, VOL. XXXIV, No. 203.—NOVEMBER, 1912.

ous shale with many characteristic Onondaga fossils. Various sections extending from New Jersey to Tennessee are described by the author and the local faunules recorded on pages 23-53. In these strata Kindle notes about 115 species, and of these 7 are described as new. Some of the Onondaga guide fossils are: *Cystodictya gilberti*, *Stropheodonta patersoni*, *Spirifer acuminatus*, *Anoplotheca acutiplicata*, *Odontocephalus selenurus*, and *O. ægeria*. On the other hand many Marcellus forms appear in these Onondaga shales, as *Strophalosia truncata*, *Buchiola halli*, *Pterochaonia fragilis*, *Actinopteria muricata*, *Styliolina fissurella*, *Tentaculites gracilistriatus*, *Bactrites aciculum*, and *Agoniatites expansus*. The greatest number of long-ranging species are, however, from the Oriskany, and if it were not that these shales occur above this sandstone the author remarks that "much paleontologic evidence could be adduced for considering the fauna to be of Oriskany age" (54).

He says further: "The eastern shore line of the Onondaga sea trended southwestward across north-central New Jersey and southeastern Pennsylvania. It probably traversed the States of Maryland and Virginia near the present axis of the Blue Ridge. From southwestern Virginia this shore line appears to have trended westward not far from the Kentucky-Tennessee line as far as the valley of Tennessee River, where it resumed its southerly trend" (65).

C. S.

4. *Preliminary report on the geology of the coastal plain of Georgia*; by OTTO VEATCH and LLOYD WILLIAM STEPHENSON. Bulletin No. 26, Geol. Surv. of Georgia, 466 pages, 30 plates, 1911.—This very valuable and detailed report is a result of the coöperative work of the Geological Survey of Georgia and the U. S. Geological Survey. The Assistant State Geologist, Mr. Veatch, describes on pages 25 to 57 the physiography of the state, and on pages 58 to 65 presents a general statement of the geology of the coastal plain, a series of sedimentaries aggregating over 4500 feet in maximum thickness. The remainder of the volume, by Doctor Stephenson, presents a great mass of desirable detail regarding the physical character, thickness and fossils of the seventeen formations composing the Lower and Upper Cretaceous and Cenozoic deposits of Georgia; their relationship to similar strata throughout the eastern Gulf area is also given. The book is an invaluable guide to the coastal plain stratigraphy not only of Georgia but as well of the entire eastern Gulf area.

C. S.

5. *Classification of the geologic formations of the state of New York*; by C. A. HARTNAGEL. Handbook 19, N. Y. State Museum, 96 pages, 1912.—In this very handy booklet are briefly defined the various geologic formations of the state of New York, about 200 in number, the majority of which make up the "standard Paleozoic section" of that state. There are of Precambrian 20+ terms, Paleozoic 153, Mesozoic 11, and Cenozoic 7. This is the third edition of Handbook 19 and all stratigraph-

ers will be thankful to the New York State Survey and to Mr. Hartnagel for this up-to-date index. C. S.

6. *Central Connecticut in the geologic past*; by JOSEPH BARRELL. Proceedings and Collections, Wyoming [Pa.] Historical and Geological Society, XII, 30 pages, 9 figs., 1912.—A popular statement, with much original matter, of the geologic history of the Connecticut valley. All teachers of historical geology will be interested in the idealized structure sections, of which there are nine, visualizing in graphic form the chief geologic events of central Connecticut since late Paleozoic time. C. S.

7. *Eighth Report of the Director of the Science Division, New York State Museum*, JOHN M. CLARKE, Director. Museum Bulletin 158; 217 pages, many illustrations, 1912.—Besides the annual report of the Director of the New York State Museum and of the Botanist, Entomologist and Zoologist, and of the archeology section, this volume contains the following papers of a geologic nature:

"Notes on the geology of the Gulf of St. Lawrence," by Dr. Clarke, describes the *demoiselles* of Entry Island, one of the Magdalens; the long Silurian Black Cape section of Cascapedia Bay, a section of about 7000 feet in thickness; and a striking unconformity between the nearly horizontal Bonaventure (Lower Mississippian) and the nearly vertical Silurian strata at Little River East, Gaspé. L. Hussakof describes three Upper Devonian fishes from Scaumenac Bay, Quebec. These are an almost complete specimen of *Coccosteus canadensis*; *Eusthenopteron foordi*, nearly 3 feet long; and *Scaumenacia curta*. R. Ruedemann has a "Note on a specimen of *Plectoceras jason*." C. H. Smyth treats of the genesis of the pyrite deposits of St. Lawrence County. The Director also describes and illustrates a recent remarkable find of more than 400 specimens of the Middle Devonian starfish *Palæaster eucharis*, from Mt. Marion near Sauger-ties, New York. C. S.

8. *Beiträge zur Kenntnis der marinen Mollusken im west-europäischen Pliocänbecken*; by P. TRESCH. Mededeelingen van de Rijksopsporing van Delfstoffen, No. 4, 96 pages, 1 map, 1912.—The introductory sixteen pages describe the character of the Pliocene deposits of the Netherlands, and the remainder of the work is occupied by an annotated list of the fossils and their distribution, recording 248 species. C. S.

9. *Canada Department of Mines*.—Recent publications of the Canada Department of Mines (see vol. xxxiii, 289) are as follows: (1) GEOLOGICAL SURVEY BRANCH; R. W. BROCK, Director.

Memoir No. 18. Southern Vancouver Island; by CHARLES H. CLAPP. Pp. 208; 18 plates, 3 figures and map.

No. 21. The Geology and Ore Deposits of Phoenix, Boundary District, British Columbia; by O. E. LEROY. Pp. 110; 7 plates, 18 figures and 2 maps.

No. 24-E. Preliminary Report on the Clay and Shale Deposits

of the Western Provinces; by HEINRICH RIES and JOSEPH KERLE. Pp. 231; 41 plates, 10 figures, and 4 maps.

No. 28. The Geology of Steeprock Lake, Ontario; by ANDREW C. LAWSON. Notes on Fossils from Limestone of Steeprock Lake, Ontario; by CHARLES D. WALCOTT. Pp. 23; 2 plates.

In the MINES BRANCH, EUGENE HAANEL, Director.

Annual Report on the Mineral Production of Canada during the Calendar Year 1910. JOHN McLEISH. Pp. 328. Also Preliminary Report for 1911. Pp. 24.

An investigation of the Coals of Canada with reference to their Economic Qualities: as conducted at McGill University, Montreal. In six volumes. By J. B. PORTER and R. J. DUBLEY, assisted by T. C. DENIS, EDGAR STANSFIELD, and special assistants. Vol. I, pp. xxiii, 232; 45 plates, 31 figures and 5 maps. Vol. II, pp. xiii, 189; 17 plates, 25 figures.

Mica: Its Occurrence, Exploitation, and Uses; by HUGH S. DE SCHMID. Pp. xiv, 411; 38 plates, 67 figures and 22 maps. This report is a second edition of the earlier one by Fritz Cirkel, issued in 1905 (see vol. xxi, p. 405). The mica production, which had a total value of about \$1,800,000 in 1906 and 1907 for the three countries from which the world's supply chiefly comes, fell to less than \$600,000 in 1909, and \$745,000 in 1910. Of this last amount, \$337,000 was the production of the United States, \$265,000 of India, and \$153,000 by Canada. The two former countries supply chiefly muscovite, while Canada produces chiefly phlogopite, or so-called amber mica. The prominent use of mica at present is in the manufacture of electric machinery; the possibility, however, of replacing mica plates by sheets of mica board ("micanite") made of thin broken fragments threatens to further demoralize the market, since it makes possible the use of much cheap material obtained from India. The scientific interest of the present volume is largely in the minute description of the many Canadian deposits in Quebec and Ontario, both from the geological standpoint and with respect to associated minerals.

Report on the Utilization of Peat Fuel for the Production of Power; by B. F. HAANEL. Pp. 145; 10 plates, 17 figures and 17 diagrams. This is a record of experiments made at the Fuel Testing Station at Ottawa, 1910-1911.

Bulletin No. 6. Diamond Drilling at Point Mamainse, Province of Ontario; by ALFRED C. LANE. Introductory by ALFRED W. G. WILSON. Pp. 59, vi, with 5 plates, one figure, and one map.

Catalogue of Publication of the Mines Branch, 1907-1911. Pp. 135.

10. *Geological Survey of New Jersey*.—HENRY B. KÜMMEL, State Geologist. Bulletin 6; pp. 82, 4 plates; Bulletin 7, pp. 37. —The annual administrative reports of the State Geologist opens this bulletin 6, which also contains a report on the improvement on the Shark River Inlet. Bulletin 7 contains an account of the

mineral industry of the state by the State Geologist. The total value in 1911 amounted to \$37,700,000, with clay and allied products first at nearly \$19,000,000, zinc mining at nearly \$9,000,000, and the Portland cement at \$3,260,000.

11. *On the Origin of the Himalaya Mountains, a Consideration of the Geodetic Evidence*; by Colonel S. G. BURRARD, C.S.I., R.E., F.R.S., Surveyor General of India. Professional Paper, No. 12, Survey of India, Calcutta, 1912. Pp. 25, pls. II.—In this paper the facts regarding the density of the subcrust beneath the several regions of northern India are concisely summed up, and the arguments throughout are clear and terse, which explains the apparent brevity of the paper. The most significant fact from the author's standpoint is the existence of a narrow subcrustal zone of remarkable deficiency of density skirting the southern base of the Himalayas. Between two stations twenty-five miles apart the deflection changes 45". The change calculated from the uncompensated topographic features would be but 25". On Hayford's hypothesis of isostasy it would be but 15". The actual change thus gives remarkably large and unexplained residuals. It is shown that this cannot be explained from the lighter specific gravity of the trough of alluvium which lies in front of the mountains unless this were enormously deep. It is also shown that a horizontal displacement of compensation within a depth of seventy-six miles does not explain it.

Colonel Burrard then advances the hypothesis of a great subterranean rift. He considers that the subcrustal shell has cracked; the northern portion, beneath the Himalayas, has shrunk and in so doing has wrinkled the upper crust, at the same time leaving a profound crack on the south which has become filled with alluvium. In comment it may be said by the reviewer that if the crack be assumed deep enough and the alluvium retains its light surface density to an indefinite depth such a hypothesis would explain the deficiency of mass, but it involves a mode of operation which is more difficult to account for and more in unexplained opposition with the conclusions regarding the deeper crust than is the fact of the deficiency of mass. It involves horizontal tension under the northern side of the Indo-Gangetic plain, enormous horizontal compression immediately north without adequate mechanical explanation, an absence of consolidation of sediment with depth and a volume of sediment which is unexplained. It seems to the reviewer, therefore, that although Colonel Burrard has made an admirable statement of geodetic facts, his explanation is wholly undemonstrated from the geologic standpoint. The possibilities do not seem to be exhausted in the several hypotheses stated and the remarkable distribution of underground densities, to the knowledge of which Colonel Burrard has contributed, offers an inviting field for investigators.

J. B.

12. *Rocks and their Origins*; by GRENVILLE A. J. COLE, Professor of Geology in the Royal College of Science for Ireland.

Pp. 175, figs. 20. New York, 1912 (Cambridge University Press ; G. P. Putnam's Sons).—This book, as stated in the preface, "is intended for those who are not specialists in geology, and it may perhaps be accepted as a contribution for the general reader." Besides a description of the composition of the chief rock types, a full discussion is given of the manner of origin, the manner of weathering, the types of scenery with which the rocks are associated. The geologic meaning of the rocks is thus brought out, and those features emphasized which are of chief interest, apart from the mere classification which is a chief aim of so many texts. It should serve to stimulate a general interest in the earth and its history, presenting the subject of the description of rocks in a most attractive and significant manner.

J. B.

13. *The Origin of Earthquakes*; by CHARLES DAVISON, Sc.D., F.G.S. Pp. 144, figs. 26. New York, 1912 (Cambridge University Press ; G. P. Putnam's Sons).—This is one of the Cambridge manuals of Science and Literature. It is clearly written, free from technicalities, and available for the general reader. The fact that the author is a well-known student of earthquakes gives it in addition an authoritative character. Earthquake phenomena are described and examples are given of different classes of earthquakes. The inferences as to origin are discussed and the part which they play in earth movements.

J. B.

14. *The Identity of Parisite and Synchisite*; by C. PALACHE (communicated).—In a paper published in this Journal last year, by Warren and Palache, describing the Quincy pegmatites, the parisite of that locality was described fully and it was shown that in all probability the mineral synchisite from Narsarsuk, Greenland, was identical with it. This conclusion was not accepted by the discoverer of the latter mineral, Dr. Flink, and he requested a new analysis of synchisite for which he supplied material to Dr. Warren. This analysis has not been made; but meanwhile the investigation has been completed elsewhere.

E. Quercigh* has shown that the supposed chemical differences between the two minerals are due to alteration products contained in the analyzed synchisite; that pure synchisite has the same formula as parisite; the same indices of refraction; and the same specific gravity. All grounds for maintaining the distinction between the two are thus removed.

The refractive indices, measured on prisms, are probably more accurate than those previously recorded.

Refractive indices of Parisite, Sodium light.

	Muso	Narsarsuk (Synchisite)	Quincy
	Quercigh	Quercigh	Warren
ϵ	1.7712	1.7690	1.757
ω	1.6717	1.6730	1.676

* Sulla identita della Sinchisite con la Parisite. Rend. d. R. Accad. Lincei xxi, 581-588, 1912.

15. *Introduction to the Study of Minerals*; by AUSTIN FLINT ROGERS. Pp. xx, 522; 591 figures. New York, 1912 (McGraw-Hill Book Company).—The number of text-books on mineralogy has been much increased in recent years, and among the additions made to the literature the present volume deserves commendation for the care with which the material has been selected so as to present in a single volume, capable of being carried in the pocket, all that is most essential for the student, both in his classroom work and in the field. The subject of crystallography occupies the first hundred pages, and, although brief for a rather advanced discussion covering the entire ground, will answer the needs of a student with the help of the teacher. The next hundred pages are given to the physical and chemical characters, following which we have a series of six determinative tables. Then comes the description of two hundred prominent species, about half of these being treated in greater detail; the rarer species are omitted entirely. The concluding pages are devoted to the subject of occurrence and association and the uses in the arts. A glossary of mineral terms is a useful feature of the work. The illustrations are mostly new and well drawn and engraved.

III. ZOOLOGY.

1. *Outlines of Evolutionary Biology*; by ARTHUR DENDY. Pp. xiv, 454, with 188 figures. New York, 1912 (D. Appleton and Company).—In many of our secondary schools and in some of our colleges the subject of biology is taught by a study of a number of different kinds of plants and animals, or in some cases of animals alone. Certain institutions offer separate courses in zoology and botany as elementary studies, although in recent years there has been a growing tendency in some of the best universities to give an introductory course embracing the general biological principles rather than the study of specific types of animals and plants. The nature of the vital processes in all organisms is made the basis of the work. This study may be followed later by the general courses in zoology and botany.

It is for such an introductory course that this book is planned. It contains no general descriptions of plants or animals, but consists rather of a discussion of general biological phenomena and the laws and theories relating thereto.

With this modern conception of the subject of biology, the book is divided into five parts, treating different phases of the subject.

Part I embraces such subjects as the nature of life; the essential functions of living things; the properties of the living substance; the relationships of all organisms; differentiation and co-operation of cells and organs; the transition from unicellular to multicellular organisms; the general development of organisms; cell structure, physiology and reproduction.

Part II includes an account of sexual phenomena in plants and animals ; the origin and development of the germ cells ; sex differentiation and inheritance ; and the evolution of sex.

Part III is devoted to variation and heredity, and Part IV to the adaptation of organisms to their environment, and the evidences of organic evolution as revealed by a study of comparative anatomy, embryology, and paleontology.

Part V, on the factors of organic evolution, discusses the more important theories of evolution, concluding with the evidence as to the ancestry of man.

The book is written in an entertaining style and, with the exception of the discussion of the evidence as to the inheritance of acquired characters, is free from personal bias. W. R. C.

2. *College Zoology* ; by ROBERT W. HEGNER. Pp. xxiv, 733, with 553 illustrations. New York, 1912 (The Macmillan Company).—While this is essentially a systematic treatise on the more important groups of the animal kingdom, it differs from most text-books of zoology in emphasizing the physiological rather than the morphological aspects of the subject. Structural details are given only as far as is necessary for a clear understanding of the relationships of the different groups. Of the numerous illustrations the majority are taken from our native species. Emphasis is laid on the economic importance of the various groups and species, and, in order to increase the general usefulness of the work, more attention is paid to the vertebrates than to the other phyla.

In each phylum a single species of the greatest importance is chosen as a type and described in some detail before taking up the systematic account of the various groups included. The same system is followed for the classes of vertebrates. W. R. C.

3. *Le Zebre : Studio Zoologico popolare* ; by Dr. ACHILLE GRIFFINI. Pp. xxvii, 298. Milan, 1913 (Ulrico Hoepli).—The Hoepli manuals, of which this little volume is one of the 1200 already published, consist of treatises on all branches of science, art, literature, and industries. They are all written in popular Italian language by authorities in the various branches of knowledge. This book contains an account of all the known species and varieties of the zebra, with information concerning those specimens which have been kept in various zoological gardens and the hybrids which have been secured from them. W. R. C.

4. *Principles of Economic Zoology* ; by L. S. DAUGHERTY and M. C. DAUGHERTY. Pp. vii, 410, with 301 illustrations. Philadelphia and London, 1912 (W. B. Saunders Company).—This is essentially a condensed Natural History of Animals, with special reference to those of economic importance. In addition to a brief description of the structure, habits, and economic relations of each of the important groups of animals, there is given, in smaller type, a vast amount of information concerning the natural history of numerous individual species.

The book is designed for use as a text in a course in zoology where the relations of animals to human interests are emphasized.

W. R. C.

5. *Elementary Entomology* ; by E. DWIGHT SANDERSON and C. F. JACKSON. Pp. vii, 372, with 496 illustrations. Boston and New York (Ginn and Company).—This book is especially adapted to the needs of students in agricultural and other colleges for a text-book to accompany a short course in the elements of entomology. The authors are practical entomologists, and this book deals with the practical rather than the theoretical side of the subject. It furnishes an excellent introduction to such courses in economic entomology as may follow, and it will also be found to supply the general reader with the essential facts regarding the structure, life-history, and classification of insects.

The attractive appearance of the book and the excellence of the very numerous illustrations should arouse a wider interest in insect study. It is such a book as the school-boy interested in out-of-door life will delight in using for the identification of his "specimens" and for information as to their ways of life.

As is the case with so many first editions under joint authorship, minor discrepancies in statement occur. There are also conspicuous orthographical errors.

W. R. C.

IV. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *Publications of the Carnegie Institution of Washington*.—Recent publications of the Carnegie Institution are noted in the following list (continued from vol. xxxiii, p. 385):

No. 74. *The Vulgate Version of the Arthurian Romances* : edited from Manuscripts in the British Museum by H. OSKAR SOMMER. Volume V. *Le Livre de Lancelot del Lac*. Part III, pp. 474.

No. 85. *Index of Economic Materials in Documents of the States of the United States*. Ohio 1787–1904. Part I, A to F, pp. 1–638. Part II, G to Z, pp. 639–1136, 4to. Prepared for the Department of Economics and Sociology of the Carnegie Institution of Washington by ADELAIDE R. HASSE. 1912.

No. 149, Part II. *The Production of Elliptic Interferences in relation to Interferometry* ; by CARL BARUS. Pp. vi, 79–168 ; 29 figures.

No. 150. *Guide to the Manuscript Materials relating to American History in the German State Archives* ; by MARION D. LEARNED. Pp. vii, 352.

No. 152. *Studies in Luminescence* ; by EDWARD L. NICHOLS and ERNEST MERRITT. Pp. vi, 225 ; 187 figures.

No. 153. *The Influence of a Magnetic Field upon the Spark Spectra of Iron and Titanium* ; by ARTHUR S. KING. Pp. 66 ; 6 plates, 4to. *Papers of the Mount Wilson Solar Observatory*, Vol. II, Pt. I.

No. 164. *A Physical Study of the Firefly* ; by WILLIAM W. COBLENTZ. Pp. 45 ; one plate, 14 figures.

No. 166. *The Composition of the Atmosphere with special*

reference to its Oxygen Content; by FRANCIS G. BENEDICT. Pp. 115; one plate. This investigation confirms the conclusion as to the essential constancy in the oxygen percentage of outdoor air. The experiments extended over a period of nine months, during which this constancy was maintained through all changes of the weather as to air-pressure, temperature, humidity, and other important conditions. The average of 212 analyses of air from near the Nutrition Laboratory showed 0.031 per cent of carbon dioxide and 20.938 per cent of oxygen; observations over the ocean gave respectively 30.936 per cent (Montreal-Liverpool, 7 anal.) and 20.932 per cent (Genoa-Boston, 36 anal.); while at Pike's Peak the result was 20.927 per cent (9 anal.). The extraordinary rapidity with which local variations, for example, in a city, are equalized was shown by observations on street air, which indicated but a slight trace of oxygen deficit; even in the Boston subway at 9.30 A. M., the only changes were a rise of the carbon dioxide to .065 per cent and a fall of the oxygen to 20.897 per cent.

No. 167. A Bicycle Ergometer with an Electric Brake; by FRANCIS G. BENEDICT and WALTER G. CADY. Pp. 111, 44, with 16 figures.

2. *British Association for the Advancement of Science*.—The eighty-second meeting of the British Association was held at Dundee during the week beginning with September 4; the registration at the opening reached the large number of 2379 members. The address of the President, Professor E. A. Schäfer, on the "nature, origin and maintenance of life," has attracted much attention.

3. *Introduction to Agricultural Mycology*. 1. *Soil Bacteriology*; by Dr. ALEX. KOSSOWICZ. Pp. 143, 47 illustrations. Berlin, 1912 (Gebrüder Borntraeger).—This is the first of two volumes by the author on agricultural mycology. It consists of four parts: The rôle of the elements (C, O, H, N, S, P and Fe) under the influence of micro-organisms; the mycology of the soil; the mycology of manure; and the influence of the micro-flora on the soil. The book abounds in literary references, which alone should make it a valuable publication. It is a thorough compilation of important data. Special emphasis is placed on the chemical changes which take place in the soil through the agency of moulds and the lower and higher forms of bacterial life. The book should prove to be of much value to the student of soil chemistry and bacteriology.

L. F. R.

4. *Catalogue of 9842 Stars, or all Stars very conspicuous to the naked eye, for the Epoch of 1900*; by W. T. BACKHOUSE, West Hendon House Observatory. Pp. xx, 186, 4to. Sunderland, England (Hills & Co.).—This very handsome volume is published to accompany a set of 14 large stars maps on the gnomonic projection (a projection from the center of the sphere onto planes tangential to the surface). The whole work is designed for use in observations of meteors, and the greatest care has been exer-

cised over every detail to secure the best results for this purpose. The arrangement is by constellations. The designation of the star is given as it appears in six different catalogues, and its magnitude as the average of from 2 to 12 different determinations.

The maps have been engraved on copperplate with the greatest precision. The reticulation is into degree spaces and the lines of projection have been drawn directly on the plates by a machine specially designed for the purpose. The boundaries of the constellations and the names of stars and constellations are printed in red from a separate set of plates. No pains have been spared to make the work the most convenient possible for the purpose intended, and the result leaves nothing to be desired. W. B.

5. *Science Manuals*.—The following are the titles of several elementary volumes in science issued by the Cambridge University Press (G. P. Putnam's Sons, New York, 40 cents each):

Life in the Sea; by JAMES JOHNSTONE. Pp. vi, 150; 4 figures.

Primitive Animals; by GEOFFREY SMITH. Pp. x, 153; 25 figures.

Links with the Past in the Plant World; by A. C. SEWARD. Pp. viii, 142; 20 figures.

An Introduction to Experimental Psychology; by CHARLES S. MYERS. Pp. vi, 156; 20 figures.

OBITUARY.

DR. LEWIS BOSS.—With the death of Professor Lewis Boss, director of the Dudley Observatory, Albany, N. Y., on October 5, in his sixty-sixth year, America loses its foremost representative of the old school of astronomy of precision. After rendering strenuous practical service on the U. S. Northern Boundary Commission, he deduced his Catalogue of Declinations of Standard Stars embodying new and authoritative ideas on the Systematic Corrections to Star Catalogues. Appointed to the charge of the Dudley Observatory, he carried out with almost unexampled rapidity and precision one of the zones for the great international undertaking of the Astronomische Gesellschaft's catalogue.

Occupied mainly throughout his life with investigations of fundamental star positions, and publishing a valuable Preliminary Catalogue in 1910, he planned a comprehensive campaign which he was at last, at the age of sixty, enabled to inaugurate with the aid of the Carnegie Institution. Infusing his energy into his staff, the observational work in the Southern Hemisphere (at San Luis, Argentina) was accomplished in an incredibly short time and it is sad beyond words that he was not fated to see the final goal of his labors attained. Undoubtedly, however, he has left the work in such shape that others may finish it on the plans he has carefully outlined. W. L. E.

W. J. MCGEE, the geologist and anthropologist, whose death occurred on September 4, was a self-made man of varied gifts and strong individuality; beginning life as a worker on a farm, by his ability and force of character he made for himself a prominent place as a scientific investigator. Of formal schooling he had but little, but he carried on his private studies in leisure hours, and thus fitted himself for work in law and surveying. Geology early interested him and his first extensive investigation was a survey of Northeastern Iowa; in 1881-82 he also made a report on the building stones of Iowa for the Tenth Census. When thirty years old, he became connected with the U. S. Geological Survey, working in the southeastern part of the United States, where he was engaged for several years in mapping an area of 300,000 square miles. He devoted himself particularly to surface and glacial geology, and the pages of this Journal between 1878 and 1892 contain numerous articles by him on these and allied subjects. He was the first president of the American Anthropological Society and had much to do with its organization. In 1885 he published a geological map of the United States and later he gave a report on the Charleston earthquake of 1886. In 1893 he joined the Bureau of Ethnology, as ethnologist in charge, and for ten years his work was largely in this field: an exhaustive investigation of Tiburon island, Gulf of California, was one of his most important labors. In 1903 he took charge of the department of Anthropology of the St. Louis Exhibition of 1904 and produced remarkable results. In 1907 he was appointed a member of the Waterways Commission, and of this body he was secretary at the time of his death. Thus his activity extended over the fields of geology, anthropology, and hydrography.

His personality was decided, perhaps aggressive, and on many points both within and outside the scientific field he held original views, but his energy and ability were never questioned. It could hardly be a surprise to those who knew him that in his will he left his body to a medical school for dissection, and directed also that his brain be used for study and preservation for the cause of science.

DR. MORRIS LOEB, Professor of Chemistry in New York University, died on October 8 at the age of forty-nine years. He was early associated as assistant with Dr. Wolcott Gibbs of Harvard University and followed him later in his own researches on complex inorganic salts; his work also extended into other lines. He was a member of the Board of Education, and was active in philanthropic work in New York City and elsewhere; among numerous generous gifts he presented \$50,000 to Harvard University in 1911 for the Wolcott-Gibbs Library.

New Circulars.

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HOW AN INSPIRATION BECAME AN ACTUALITY.

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[FOURTH SERIES.]

ART. XLIII.—*A Buried Wall at Cuzco and Its Relation to the Question of a pre-Inca Race (Yale Peruvian Expedition, 1911)*; by ISAIAH BOWMAN.

DURING the summer of 1911 the Yale Peruvian Expedition spent some time studying the surroundings of Cuzco, and in a ravine* on the outskirts of the city came upon a group of facts in relation to a buried wall that appear to have a large significance. The wall belongs to the older type of rougher and apparently more primitive architecture which students of Peruvian archeology have for some time been inclined to regard as pre-Inca, though the belief has heretofore not depended upon secure evidence. It appears that we now have a fairly safe basis for concluding that the wall is pre-Inca, that its relations to alluvial deposits which cover it indicate its erection before the alluvial slope in which it lies buried was formed, and that it represents the earliest type of architecture at present known in the Cuzco basin.

The wall extends along the border of a ravine on the southwestern edge of Cuzco, BM₁—BM₁₀, fig. 1. The detailed topographic features are brought out in figs. 2 to 5. The lower end, BM₁₀, fig. 1, is now almost entirely uncovered; the upper and middle portions are deeply buried in coarse but well-stratified gravel of prehistoric though postglacial age. A cross-section of the alluvium in which the wall lies buried, fig. 2, gives one a clear idea of its peculiar position. The ravine itself is relatively new, fig. 5, and we were told that it had been opened, at first artificially, about ten or twenty years ago.

* It was in a neighboring ravine that the vertebrate remains were found which have been described in earlier papers in this Journal, vol. xxxiii, pp. 297-333, 1912. See these papers also for a preliminary statement on the buried wall and related facts.

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Clearly from its present condition it has been enlarged and made irregular in detail through water action extending over a short period of years. Though the material exposed along the banks and the adjacent slopes is gravel, it stands up in steep and, in many places, vertical bluffs. Its recent origin is also indicated by the rapidity with which the stream, now running through the ravine in wet weather, is cutting its banks and carrying away alluvial material. The wall, therefore, has no

FIG. 1.

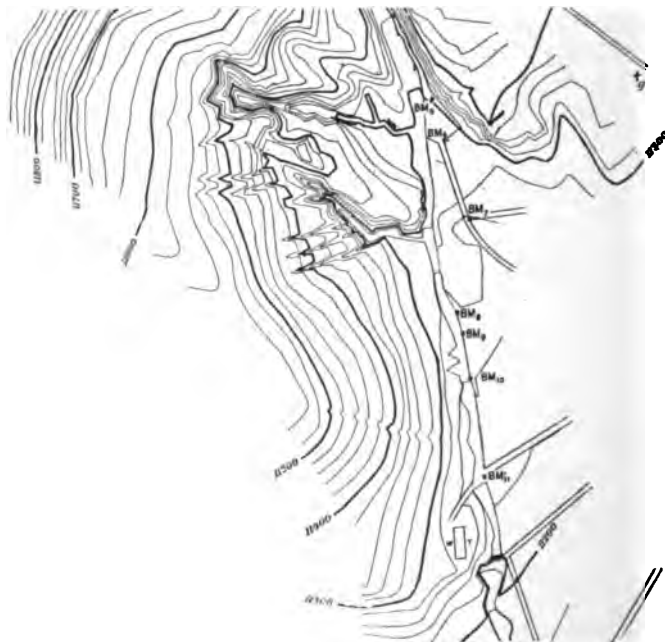


FIG. 1. Ayahuaycco Quebrada, near Cuzco, Peru, surveyed and drawn by Kai Hendriksen. [From this Journal, vol. xxxiii, Plate II, Contributions of the Yale Peruvian Expedition of 1911.]

Altitudes based on railroad survey. Contour interval, 20 feet. Scale about 800 ft. to 1 inch.

necessary relation to the ravine as an artificial canal, though the ends of the wall perhaps afforded modern man a clue to an earlier relation between a now buried canal and the wall.

The main facts calling for explanation are as follows:

(1) The buried wall runs, not down, but at right angles to an alluvial slope.

(2) It is made of blocks of cherty limestone which have been cut and fitted in a rough manner, giving a face as shown in

fig. 6. Both the face toward the ravine and the face in contact with the gravel consist of cut stone.

(3) The wall is covered at one point with six feet of stratified gravel. Stratified gravel also faces the ravine side of the wall at "A," fig. 2.

(4) On the down-slope side, fig. 6, stratified gravels may also be seen abutting sharply against the wall wherever portions of it were removed.

(5) The wall does not now conform to the alluvial grade of the surface of the deposits in which it lies buried, nor to the gradient of the ravine floor, being less steep than the surface of the alluvium and steeper than the present channel.

(6) The deposits in which the wall is buried form part of a great series of deposits with comparable physiographic features, equivalent ages, and definitely determinable origin.

(7) The definitely known Inca buildings stand *upon* alluvial

FIG. 2.

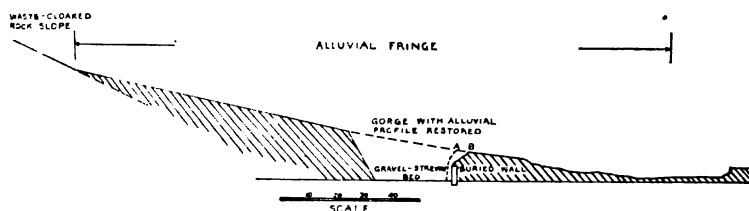


FIG. 2. Cross-section of belt of alluvium bordering the hills southwest of Cuzco. The former undissected slope and its relation to the buried wall are also shown. A and B represent the relation of the eastern border of the ravine with respect to the wall at two stations.

slopes now in process of dissection; not as in the case of the wall, *below* the level of the alluvial surface.

We shall now inspect the facts indicated above to ascertain their nature and then examine their bearing on the question of a pre-Inca race. It is not proposed to draw hard and fast conclusions. Such conclusions can be formulated only when much more field work, particularly in the way of excavation, has been done, and a larger amount of archeological data gathered. On the other hand, it is not proposed to present mere facts alone, and to shirk the responsibility of interpreting them.

At first sight the buried wall appears to be directly related to the present drainage. It forms, for a part of its length, a sort of lining to a channel along which water is now at times conveyed. Imagining small changes in stream volume from time to time, one reaches the temporary conclusion that in times of high water a deposit would form on the inside (stream

side) of the wall. In later periods of low water, these deposits might in turn be cut partly away. Such an argument calls for no pronounced modifications of prevailing climatic conditions, associates the wall with existing topography, and is the most natural explanation following a first inspection of the field. Further consideration of the conditions leads one to take a quite different view from the one outlined. Difficulties arise which appear to be solved only by more radical explanations.

In the first place, if the wall were built as a lining to the existing ravine, why was its eastern face, fig. 6, made of dressed stone? One does not find this condition prevalent

FIG. 8.

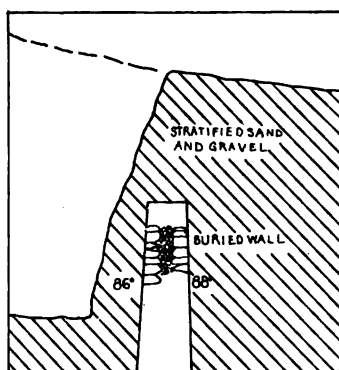


FIG. 8. Details of inner structure of the buried wall in enlargement of A, fig. 2.

among walls facing the *andenes* or artificial terraces about Cuzco. I have seen it in a few walls, though under circumstances leading one to suppose that the prominent position of the wall called for greater care, indeed almost needless care, in its construction. About the only purpose a faced wall would serve on a terrace scarp would be to strengthen the wall against the strain imposed by the soft earth behind it. We must grant, however, that the existence of a faced wall is not in itself conclusive proof of unusual relations.

On the other hand, we have in the stratified gravels that abut sharply against the outer face of the wall a condition of a totally different nature. The wall was carefully removed, stone by stone, leaving the gravels undisturbed for a photograph, fig. 6, in which the stratification is clearly apparent. But stratification may also show on the upper side of a terrace wall since the constant movement of irrigation water down the

slope of the terrace accumulates sand and gravel on the upper side of the wall. It should be noted, however, that the buried wall is faced not only on its upper, but also on its lower side by stratified gravels at least 15, and possibly 40 or 50 feet thick. Irrigation can not account for the material since it would here imply the up-hill flow of water. The difficulty disappears if we apply the hypothesis of burial by aggradation from above, and have the material move down the slope of the alluvium (fig. 2).

FIG. 4.



FIG. 4. The alluvial fringe in which lies the buried wall. The waste-cloaked rock slope of fig. 2 is on the right; the alluvium begins on the line marking the change of gradient. The Cuzco basin and the western border of the city of Cuzco in the middle distance.

It is indeed the slope of the alluvium that has the most striking relation to the buried wall. It is a smooth slope with an entirely normal appearance. It breaks distinctly with the thinly-cloaked rock slope from which its material was chiefly derived; and when the plane of the slope is continued downward it is seen to correspond in level with the slope on the opposite side of the ravine. Furthermore, the lower section of the slope has a flatter gradient than the section above in the manner of alluvial material accumulated under natural conditions. Beyond the wall (right, fig. 2) the natural alluvial slope becomes broken, in some places almost at the wall, in others some yards away. The irregularities are caused by artificial excavation, by breaks in the wall, which have permitted the

water of the ravine to escape and erode the gravels, and by the natural effects of continued cultivation and irrigation away from the higher edge of a terrace. A wall not too deeply buried in loose material with a pronounced surface slope is a defence against excessive erosion of material above it; it cannot prevent the erosion of material below it. While the terraced fields below the wall were gashed by the incipient ravines of irrigation water, the slope above the wall remained practi-

FIG. 5.



FIG. 5. The buried wall is several feet behind the gravel bank on the extreme left, looking south toward Cuzco.

cally intact. The agreement of the gradients on opposite sides of the wall as shown in fig. 1 is too close to be explained by accident; it can be explained only by assuming that both slopes are part of a general surface built up during a period of aggradation which has now given place to a period of stream dissection.

It is now necessary to consider the work of individual floods which may effect great changes in the minor slopes of the land and in the position of loose surface material. A series of floods in a succession of unusually wet years may lead to changes which appear almost cataclysmic. But the changes may be recognized as the work of sudden and unusual floods, (1) by the coarseness of the material where coarse material is available

and (2) by the immediate change from aggradation to degradation as soon as the floods cease. Now in the ravine in point the gravels are clearly coarse below, but they become finer above and the top of the section in some places exhibits finely laminated sand. Moreover, the mass of material with which the alluvium of the ravine is correlated is so great, from a few feet to 50 feet thick in places, and so widely distributed in the Cuzco basin, as to give it a much greater importance than that associated with occasional floods.

FIG. 6.



FIG. 6. Relation of the buried wall to the gravelly alluvium. A, the undisturbed wall; B, the gravel above the wall, to the right undisturbed, to the left removed since the gravel here faced the wall in addition to lying above and behind it; C, the outer layer of faced stone removed to show filling of rubble; D, the inner layer of faced stone removed and undisturbed stratified alluvium showing behind it; E, the inner face set up roughly stone by stone. The bottom of the wall lies three feet below the present channel floor in the shaded foreground of the photograph.

All about the Cuzco basin the lower slopes are composed of land waste, a great alluvial fringe or piedmont belt of alluvium which extends up the tributary valleys. In some cases the older alluvium interlocks or interfingers with glacial material

disposed in the form of terminal moraines or coarse outwash from moraines, and therefore belongs to the glacial series. The alluvium consists of a finer series below and a coarser series above. When studied in detail the deposits indicate two periods of glaciation. The alluvium of whatever kind has been eroded periodically, giving rise to a series of terraces along the streams. These vary in number according to the headwater relations of the draining streams; they also vary in width and breadth and somewhat in their position with reference to the valley mouths. In this connection it is sufficient to note that the alluvial fringe in which the buried wall occurs belongs to the last series of deposits which represent one of the last phases of broad climatic changes which culminated in the glacial period and have since declined, and is intermediate time between the climax of the glacial period and to-day. It was produced during one of the later and feebler climatic pulsations which did not lead to glaciation though they tended in that direction. If the last glacial invasion occurred 50,000 years ago, the lower terraces might be said to be formed at intervals about 30,000 and 10,000 years ago. If we accept 25,000 years as the length of the post-glacial interval, then 15,000 and 5,000 years would represent the age of the upper and lower terraces respectively, as very roughly approximated from the thickness of the deposits and the depth of erosion.

The lack of correspondence between the grade of the alluvium and the grade of the wall forms one of the strongest reasons for concluding that the wall has not been sunk into the alluvium, but has been covered by it. Fig. 2 indicates but one element of the alluvial slope; the second element is a southward descent in the direction of the wall, though with a steeper gradient. If a trench had been dug and the wall sunk into or built into it, it is clear that the same relations *might* prevail though it is unreasonable that they should prevail, unless the trench were dug in the bottom of a natural water channel eroded in alluvial material in process of dissection. The dissection would dispose the material on a flatter gradient, that is, it would decrease the gradient of the channel as compared with the gradient of the original alluvial slope. A wall then built into the channel would likewise have a flatter gradient than the alluvial slope above. The channel can not be natural however since it runs not down a slope but along it.

On the other hand, our reasoning is entirely in accord with the facts if we suppose the wall to have been built before the last period of alluviation, and with a gradient conforming to the slope of the surface. A later climatic change would then account for the beginning of aggradation and the increased

gradient of the surface. The buried channel and wall would then have flatter gradients than the surface channel and slope. Later excavation, either artificial or natural, would expose the buried wall and make apparent the discordance between two sets of things made at two different times under different conditions.

This line of reasoning is further supported by the fact that the stratified gravels abut sharply against the wall on both sides and even overtop it in an unbroken series. The wall was not built into alluvial deposits, but was covered by them after it was built. Even if a wall were built squarely against a cleanly cut gravel bank, it could not fit the face of the bank so closely but that percolating water would rearrange the material and leave, between the undisturbed stratified gravel and the wall, a zone of unstratified fill like that so often seen on the outside of an old house foundation in process of re-excavation. The difference in gradient is interpreted, then, as a condition which might be due to the building of a wall in the bottom or along the side of a ravine, were it not that the gravels abut sharply against both sides of the wall without a facing of unstratified material.

Among the facts that point to burial of the wall, a second one, the material of the alluvium, may now be considered. The wall rests upon a rather pure sand, distinctly not a gravel, as determined by excavation. Coarse gravels, however, constitute the alluvium that banks against the wall and appear in the section on the side of the ravine opposite the wall. The top of the section consists in general of finer material. In this succession of coarse and fine we have a condition in itself indicative of a change from degradation to aggradation and back again to degradation. The wall rests upon fine material accumulated at a time when wash from surrounding highlands was feeble and transportation slow; the coarser material above it represents the streams in full vigor loaded with detritus both coarse and fine which they accumulated upon a former alluvial slope; the finer material at the top represents the deposits of waning streams.

Quite apart from the repeated testimony of residents that the present channel in which the wall stands was opened in recent years, and therefore that the wall was not used as a retaining dike for terrace front or irrigating stream, is the evidence afforded by the alternating ash and sand beds in the upper few feet of the alluvial fringe. Near the lower end of the map, BM₁₁, fig. 1, the ravine cuts through a section of most peculiar composition. On the right hand side (facing down the ravine) are interstratified ashes, pottery, and bone fragments, together with pieces of charred wood, corn, and

quina. They occur to depths of several feet, the deepest burial being to a depth of about six feet. On the left-hand side of the ravine the section is earth below and ash above, and a huge ash pile on which the refuse of the city is dumped still persists, though its present use is far less extensive than formerly. From the inclination of the alternating ash and sand layers one is obliged to conclude that the ash pile existed in the form of a mound from which slopes led toward the hill as well as in the opposite direction on the farther side of the mound. No other relation will explain the dip of ash beds and sand beds *toward* the hill (west), at one place to the extent of 28 degrees, and in many cases to 10 and 15 degrees. A slight dip of several degrees could be explained by an aggrading stream working on all radii of an alluvial fan; so great a dip as 28 degrees seems explicable only on the assumption of a mound from which ash slipped and was washed on gradients up to the limits of repose.

The alternating beds represent a long period of accumulation. Only a careful study of the pottery and bone material in them will establish their age, though they date back without doubt several hundred years and the lowest may represent the accumulations of several thousands of years ago. Wash from the adjacent hill slope is very slow indeed. Only the smallest and most incipient ravines now break the smooth outline of the thinly cloaked rock slope and the alluvial fringe in front of it. The largest are but a foot or two deep. Under present climatic conditions it would appear to require at least several thousand years for the upper five or six feet of the alluvial fringe to form, for it consists on the whole of fine, not of coarse material, and in this respect is in contrast to the coarser alluvium washed down in the glacial period by vigorous streams, and probably in a relatively short time.

To produce alternating ash layers on the *south* side of the ravine would require its slopes to extend across the space now occupied by the ravine. That is equivalent to saying that during the accumulation of the ash and sand beds the ravine did not exist. We therefore conclude that the ravine is new, both from the testimony of the people and from an entirely independent line of evidence, the position and relations of the alternating ash and sand beds. There is a third independent line of argument for the youth of the ravine; its narrow, steep-walled, fresh condition in spite of the fact that its walls are merely loose sand and gravel, of all materials the most likely to slump down quickly to moderate grades. If the wall ever had served as part of a retaining dike on the border of a ravine like the existing one, such use was abandoned long before the ash beds began forming. Now if we assume a few

hundred years as the time required to produce the last few feet of the alluvial fringe, we should have to assume a much longer time for the whole fringe to form. We have already seen that the wall lies *buried in gravel*, that it was not set into gravel, but that gravel was built against it and that it therefore antedates the alluvial fringe or at least the upper fifteen or twenty feet of it.

Finally, we shall consider the fact that the alluvial fringe is being dissected and that it has for some time been undergoing dissection. It follows that to the time required to form the fringe must be added the time required to dissect it to its present condition in order to arrive at a conclusion as to the age of the wall buried in the alluvium. Here we have as yet no reliable criteria. Erosion is in progress now and is active. I think geologists would in general agree that the work of dissection in the lowest alluvial level would require at least several hundred years. If we add these hundreds to the hundreds required to form the upper part of the fringe, we shall carry the process backward at least to the time of the Spanish Conquest. I am strongly inclined to believe that when the ash beds are studied in detail the lowermost beds will represent a period decidedly earlier. If the upper layers represent hundreds of years, the thick and more extensive lower layers that surround the wall and overtop it represent thousands. According to the chronology of Markham, the first (pre-Inca) king of which legends take note reigned about 900 B. C., or roughly, 3000 years ago. If the wall were built 2000 B. C., or even 4000 B. C., that is to say, from 4000 to 6000 years ago, it would still fall within the period that the gravels appear to represent, and without the period covered by the hundred kings of legend. Not only is the wall pre-Inca; the possibility exists that it may antedate the period in which ruled the legendary pre-Inca kings.

Extensive excavation about Cuzco would no doubt reveal the older walls in relations that would establish their age in a clearer manner than in the present case. The fact that the better built walls, definitely known to belong to the Inca period, stand upon an alluvial terrace, never beneath or in the terrace material, while, as in the case of the buried wall described here, some of the cruder walls do stand buried in the alluvium, seems to indicate a marked difference in their ages, the Incas building after the last period of alluviation and before the present period of dissection set in.

This conclusion is supported by at least one fact easily gathered from the older buildings of Cuzco. It is noteworthy that the buildings in some cases consist of an upper and a lower section of different stone cut in a different manner. The

lower part of the walls in these cases is invariably of cherty limestone; the upper is of andesite. The cherty limestone is easy to work compared with the andesite and has been trimmed into blocks of irregular shape and different sizes. It is laid in tiers of decidedly greater irregularity than may be observed in the andesite blocks above. Furthermore, the blocks of the lower walls are not now in alignment everywhere, but have suffered both horizontal and vertical changes of position, or were originally built more irregularly than the upper parts of the walls of different material. The upper parts of the walls, on the other hand, are decidedly regular and in most cases fairly straight, even when built upon lower walls of irregular trend. The rougher blocks of the lower wall are in many places displaced and built into the upper wall. It is clear in other cases that rebuilding has been done sometimes to the extent of repairing a breach in the lower wall by the use of better hewn blocks of the upper wall. I have never been able to find blocks of the upper wall enclosed in undisturbed blocks of the lower wall. We have then a set of facts clearly trending in the direction of the conclusion that the limestone walls are old and the andesite walls are new, relatively.

Other deductions should also be noted which appear to point to the same conclusion. The limestone is easier to work than the andesite, but it cannot be wrought into blocks of such perfect shape and with such smooth surfaces. It is brittle and flakes unevenly. Though built into a solid and remarkably tight wall (considering the absence of mortar) yet the blocks are nowhere perfectly fitted as in the case of the andesite. Some of the latter are so finely cut that even a needle point cannot be introduced between the curved surfaces of adjacent blocks. Does it not seem natural, in view of the relative ease with which the limestone is worked, that the use of limestone should be learned before that of andesite, however defective it may be for finer uses?

The kings of Cuzco did not conquer a savage but a semi-civilized race whose domestication of the llama, the alpaca, and the dog, and whose conquest of water and the ground point to a great antiquity as that term is used in history. We need not assume a long interval between them and their mythical predecessors. The builders in the old may have become the builders in the new dynasty. Likewise under the stimulating influence of the Incas every art was rapidly advanced, great buildings arose, irrigating channels improved and extended, and, apparently, new walls built in place of or upon the old.

A great deal of further work must be done to enable us to reach satisfactory conclusions as to all the important ramifications of the problem. Of particular importance is the work of

excavation. Trenches dug in well-selected places should yield other walls with even more certain relations. The considerations presented in this paper are based upon a very small collection of facts gathered as by-products rather than as main results during a few days field work about Cuzco. If they should stimulate further work in this almost unexplored and certainly very rich field, the object of the paper will be accomplished. Certainly the temporary conclusions have a most serious bearing on an old problem whose solution should not be postponed much longer, now that a railroad makes access to these ancient treasures moderately easy.

ART. XLIV.—*Kragerite, a Rutile-bearing Rock from Krageroe, Norway*; by THOMAS L. WATSON.

Introduction.

DURING investigations, which have extended over a period of several years, of the rutile deposits of Virginia for the State Geological Survey, Frank L. Hess of the U. S. Geological Survey generously placed at my disposal for comparative study several small specimens of the rutile-bearing rock from Krageroe, Norway. Microscopic and chemical study of the rock prove it to be of unusual composition, hence a brief description of the rock with special reference to its relations in the quantitative system is considered appropriate at this time.

The results set forth in this paper are based entirely on the specimens furnished the writer by Mr. Hess, and they may or may not be wholly representative of the rock mass. The writer has no personal knowledge of the rock occurrence or of its field relations, but a communication from Professor J. H. L. Vogt of Christiania states that the rock (kragerite) has been examined by Professor Brögger, but has not been described in detail. He further remarks that the rock has been found in the neighborhood of Krageroe, but only at a single place, and it has not great areal extent. It has been worked in later years for rutile, the percentage of which is very variable.

In 1904 Professor Brögger briefly described the rock as a new member of the aplite series and named it kragerite. Through the kindness of Professor Vogt, I give a translation of the short "Besprechung" by Professor Brögger:

"Brögger discussed a new rock, kragerite, a new member of the aplite series. The rock is of practical interest on account

of its content of rutile. In theoretic connection, the speaker considered this rock, which consists almost exclusively of albite and rutile, a differentiation product of a gabbro magma, analogous to the appearance of lestiwarite, an aplitic differentiation product of a nepheline-syenite magma, etc. In addition, mention was made by analogy of routivarite, anorthosite, and oligoclasite. The content of titantic acid in the kragerite was attributed to pneumatolytic processes during formation."

Petrographic Character.

General description.—The rutile-bearing rock (kragerite) from Krageroe, Norway, submitted to analysis is medium-grained and of light color, with a pronounced granitic habit. Its most prominent megascopic constituents are light gray and pinkish feldspars and nearly black rutile, with a little quartz. Several small areas of a green ferromagnesian mineral, probably pyroxene partly altered and associated with rutile, were noted. The feldspar and quartz grains measure 1 to 2^{mm} in cross-section; the rutile grains rarely exceed 1^{mm} and many are less than 0.5^{mm}. The quantity of nearly black rutile and the pink color of a part of the feldspar increase the depth of color of the rock. Most of the feldspar shows fine albitic twinning on cleavage surfaces under a pocket lens. The rutile is in small grains, partly disseminated through the rock, but mostly segregated along roughly parallel lines which give it a streaked or banded appearance, and which Professor Brögger refers to as *schlieren* of local enrichments of the mineral.

Microscopic description.—A thin section of the less rich rutile portion of the rock was examined under the microscope and found to consist essentially of feldspar, much rutile, some quartz, and a little ilmenite. No ferromagnesian silicate minerals were observed.

Feldspar is much the most abundant constituent and is composed chiefly of a sodic plagioclase (albite-oligoclase) together with some microcline and orthoclase, the latter intergrown with albite as micropertthite. Some of the feldspar anhedral show partial micropoikilitic structure developed from inclosures of other feldspar, quartz, and rutile. The feldspars are almost wholly fresh, but occasional small spots are altered to colorless mica. Partial peripheral granulation of a part of the feldspar and quartz was indicated, accompanied by slight bending of the lamellæ of several plagioclase individuals.

Rutile, the second mineral in quantity, ranges from small microscopic idiomorphic crystals to irregular massive grains about 1^{mm} in diameter. Some of the larger grains show partial crystal outline. It is deep red-brown, usually pleochroic, and frequently shows cleavage and twinning. Some ilmenite,

which at times exhibits slight alteration to leucoxene, is associated with the rutile. A single small grain of pyrite was observed inclosed in one of rutile. Apparently the rutile does not show predilection for one rock mineral more than for another. It occurs entirely enveloped by feldspar, along the sutures of feldspar individuals and of feldspar and quartz, and sometimes penetrates into the substance of both. The relations of the rutile to the silicate rock minerals suggest that it crystallized from the magma as did the feldspar and quartz,

FIG. 1.

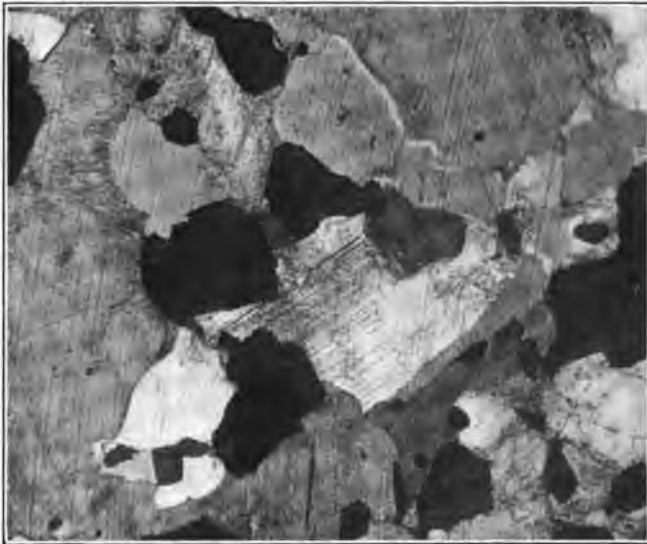


FIG. 1. Microphotograph of kragerite, a rutile-bearing aplite, from Krageroe, Norway. The black grains and crystals are rutile; other constituent is chiefly sodic feldspar. Nicols crossed. Magnified 27 diameters.

and that the usual order of crystallization was observed. These relations are shown in fig. 1, a microphotograph of a thin section of the rock.

A thin section of the rutile-rich portion of the rock, representing probably the schlieren of Professor Brögger, was studied microscopically. It was composed chiefly of rutile, together with some biotite, partly altered to chlorite, a few anhedral grains of apatite, and an altered light-colored silicate mineral, probably a potash feldspar.

In reflected light the rutile is dark brown to gray with the faintest greenish tinge; in transmitted light it is pleochroic,

usually shows cleavage and twinning, is marked by irregular fractures, and shows some alteration peripherally and along fractures to leucoxene. Inclosures of the silicate minerals, chiefly biotite, are noted in the rutile, and rutile granules are distributed through the silicate minerals—a relationship which suggests contemporaneous crystallization of the rutile and silicate minerals. Biotite, quantitatively the next mineral to rutile, of brown color, strongly pleochroic, and partly altered to chlorite, is developed in aggregates of shreds which occasionally observe a radial arrangement or grouping.

An analysis made of the rutile separated from the rock and freed as nearly as possible from silicate minerals yielded the following results:

Chemical analysis of rutile from Krageroe, Norway.

(Wm. M. Thornton, Jr., analyst.)

TiO ₂	97.68
SiO ₂	1.06
FeO.....	0.81
Cr ₂ O ₃	0.39
V ₂ O ₅	0.55

Total 100.49

Specific gravity.. 4.225 (J. Wilbur Watson)

Chemical Composition and Classification in the New System.

The chemical analysis of this rock is as follows:

Chemical analysis of kragelite from Krageroe, Norway.

(J. Wilbur Watson, analyst.)

	Per cent.	Mol.
SiO ₂	50.52	.842
Al ₂ O ₃	13.98	.137
Fe ₂ O ₃	0.49	.003
FeO.....	0.16	.002
MgO.....	0.34	.009
CaO.....	1.05	.020
Na ₂ O.....	6.18	.100
K ₂ O.....	1.00	.011
H ₂ O.....	0.20	---
H ₂ O +	0.30	---
TiO ₂	25.00	.313
V ₂ O ₅	n. d.	---
MnO.....	None	---
P ₂ O ₅	Trace	---
CO ₂	None	---
S.....	0.12	.003

Total 99.34

Calculated in the usual way from the chemical analysis of the rock given above, the composition of the feldspar content corresponds to :

Or	6.12
Ab	52.40
An	5.56
Ab, An _m ratio	9.4:1=47:5
Or-Ab, An _m ratio	1.9:5= 5:47
Total plagioclase	57.96
Total feldspar	64.08

A noteworthy feature of the rock as indicated in the analysis is the unusually large percentage of TiO₂, which is present chiefly as rutile and in very small quantities as ilmenite and leucoxene. The high Na₂O, which greatly exceeds K₂O in amount, and the low CaO confirm the microscopic study of the composition of the principal feldspar as corresponding to a sodic plagioclase of the albite-oligoclase series.

The norm as calculated from the analysis and the position of the rock in the quantitative system are as follows :

Norm.		Ratios.
Q... 7.62		
Or.. 6.12	Class, $\frac{\text{Sal}}{\text{Fem}} = \frac{72.31}{26.66} = 2.7 = 11$,	dosalane.
Ab . 52.40		
An . 5.56	Order, $\frac{Q}{F} = \frac{7.62}{64.08} = 0.12 = .5$,	germanare.
C... 0.61	Sal=72.31	
Hy . 0.90		
Hm. 0.48	Rang, $\frac{K_2O + Na_2O}{CaO} = \frac{111}{20} = 5.5 =$	domalkalic, '2=monzonase.
Ru . 25.04		
Pr.. 0.24	Subrang, $\frac{K_2O}{Na_2O} = \frac{.11}{100} = 0.11 = .5$,	persodic.
H ₂ O 0.50	Fem=26.66	
99.47		
	Grad, $\frac{P+O}{M} = \frac{0.90}{25.52} = .03 = 5$,	permitic.
	Section, $\frac{H}{T} = \frac{0.48}{25.04} = .02 = 5$,	no name.

As indicated above, the norm places the rock in the dosalane class, in the germanare order, in the domalkalic rang *monzonase*, and in the persodic subrang. Because of the unusual composition of the rock, to which attention has been directed in the analysis, it is necessary to further subdivide into grad and section. This subdivision, which shows up the peculiar composition of the rock, places it in grad 5 (permitic), and section 5.

The subdivision on $\frac{H}{T}$, which places the rock as a section of grads 4 and 5, is not provided for rocks in class II (dosalane)

of the new system. It has been found necessary to give special significance to TiO_2 in classifying rocks in which so much primary rutile* is found, such as the one forming the subject of this paper, the several types occurring in the Amherst-Nelson counties area in Virginia, and the new type *urbainite* associated with anorthosite in the Parish of St. Urbain, Quebec, Canada, recently described by Dr. Warren.†

There are tabulated in Washington's tables only four representatives of the persodic subrang of monzonase. A subrang name has not been suggested for these rocks nor does the analysis of either show the peculiarities of composition of the Norway rock. Since the Norway rock (*kragerite*) is shown to have an intermediate position in the quantitative system and on account of its unusual composition, no name for the magmatic division is suggested.

In high titanium and feldspathic content, and in being a differentiation product of a gabbro magma, the Norway *kragerite* is perhaps closest allied to the rutile-rich feldspathic syenite‡ (*piedmontose*) of Nelson County, Virginia, but otherwise the rocks bear little resemblance to one another. From their calculated norms, the two rocks fall into different classes in the quantitative system; the Norway *kragerite* is a dosalane (class II), the Virginia *piedmontose* is a persalane (class I). Both rocks are alike in occupying new positions in the quantitative system.

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University of Virginia.

* Cross, W., Iddings, J. P., Pirsson, L. V., Washington, H. S., Modifications of the Quantitative System of Classification of Igneous Rocks, Jour. of Geol., vol. xx, pp. 550-561, 1912.

† Warren, Chas. H., this Journal, vol. xxxiii, pp. 263-277, 1912.

‡ Watson, Thomas L., and Taber, S., Bull. U. S. Geol. Survey, No. 430, 1910, pp. 200-213; Bull. Va. Geol. Survey No. 111. (In press.)

ART. XLV.—*The Thermodynamics of the Earth's Non-adiabatic Atmosphere*; by FRANK H. BIGELOW.

Introduction.

THE observations in the free air of the earth, by means of balloon ascensions up to 18,000 or 20,000 meters elevation, indicate that the atmosphere does not conform to the adiabatic relations of pressure, temperature, density and gas coefficient, but that except for occasional conditions it is a nonadiabatic atmosphere. It is, therefore, necessary to derive the thermodynamic formulas in forms that are applicable to such an atmosphere, wherein the nonadiabatic relations are incessantly varying through considerable ranges. The formulas here employed have been checked in numerous ways, and they have been applied to the solution of several well-known outstanding meteorological problems, (1) the cause of the semi-diurnal waves of barometric pressure, (2) the cause of the isothermal layer in the upper levels, (3) the general circulation on a hemisphere, (4) the local circulation in cyclones and anti-cyclones, (5) the cause of the diurnal variations of the terrestrial magnetic field. In this paper our applications of the formulas will be limited to the causes of the isothermal layer.

The adiabatic and the nonadiabatic formulas.

The temperature gradients in a vertical direction are taken, $a_z = -\frac{dT_z}{dz} = -9.8695^\circ \text{C. per 1000 meters}$ for an adiabatic atmosphere; they are actually observed, $a = \frac{a_z}{n} = -\frac{dT}{dz}$ and are very variable, so that n ranges through large values, and is $n=1$ for an adiabatic stratum. Assume the following notation: T_z temperature, P_z pressure, ρ_z density, R_z gas coefficient in the Boyle-Gay Lussac Law, $P_z = \rho_z R_z T_z$, on one level, and $P = \rho RT$ on another level, as 1000 meters higher. If the acceleration of gravity is $g_z = 9.806$ meters per second, and the system of constants is that of the kilogram-meter-second system (K.M.S.), as given in Table 14, Monthly Weather Review, March, 1906, we can proceed as follows to develop the corresponding formulas. Assume (1), (2), (3), for the adiabatic and the nonadiabatic systems, respectively, and by simple substitutions the others are readily derived.

Adiabatic.

Nonadiabatic.

- | | | |
|-------------------|-------------------|-------------------|
| (1) Gravity..... | $g\rho dz = -dP.$ | $g\rho dz = -dP.$ |
| (2) Pressure..... | $P = \rho RT.$ | $P = \rho RT.$ |

*Adiabatic.**Nonadiabatic.*

$$(3) \text{ Temperature } T = T_0 - a_0 z. \quad T = T_0 - az = T_0 - \frac{a_0}{n} z.$$

$$dT_0 = -a_0 dz. \quad dT = -adz = -\frac{a_0}{n} dz.$$

$$(4) \text{ Logarithmic } \frac{dT}{T} = \frac{Ra_0}{g} \frac{dz}{P}. \quad \frac{dT}{T} = \frac{R}{g} \frac{a_0}{n} \frac{dz}{P}.$$

From formula (26) of the paper referred to above.

$$(5) \text{ Auxiliaries } \dots \frac{R}{g} a_0 = \frac{k-1}{k}. \quad \frac{R}{g} \frac{a_0}{n} = \frac{k-1}{nk}.$$

$$(6) \text{ Ratio } \dots \frac{P}{P_0} = \left(\frac{T}{T_0} \right)^{\frac{k}{k-1}}. \quad \frac{P}{P_0} = \left(\frac{T}{T_0} \right)^{\frac{nk}{k-1}}.$$

It is seen that one passes from the adiabatic system to the nonadiabatic system by the factor $n = \frac{a_0}{a}$ the ratio of the two gradients. Take the general law in two strata for the ratio,

$$\frac{\rho R}{\rho_0 R_0} = \frac{P}{P_0} \frac{T_0}{T}$$

and substitute the value of $\frac{P}{P_0}$ respectively from 6,

$$(7) \quad \frac{\rho R}{\rho_0 R_0} = \left(\frac{T}{T_0} \right)^{\frac{k}{k-1} - 1}. \quad \frac{\rho R}{\rho_0 R_0} = \left(\frac{T}{T_0} \right)^{\frac{nk}{k-1} - 1}.$$

$$\frac{\rho R}{\rho_0 R_0} = \left(\frac{T}{T_0} \right)^{\frac{1}{k-1} + 0}. \quad \frac{\rho R}{\rho_0 R_0} = \left(\frac{T}{T_0} \right)^{\frac{n}{k-1} + (n-1)}.$$

Hence we make the following important inference :

$$(8) \quad \frac{\rho}{\rho_0} = \left(\frac{T}{T_0} \right)^{\frac{1}{k-1}} \frac{R}{R_0} = 1. \quad \frac{\rho}{\rho_0} = \left(\frac{T}{T_0} \right)^{\frac{n}{k-1}} \text{ and } \frac{R}{R_0} = \left(\frac{T}{T_0} \right)^{n-1}.$$

This means that the gas coefficient R is a *constant in the adiabatic system, but it is a variable in the nonadiabatic system*. The further significance of interest is that the specific heat is a variable in the nonadiabatic air.

$$(9) \quad C_{p_0} = R_0 \frac{k}{k-1} \text{ (constant)}. \quad C_p = R \frac{k}{k-1} \text{ (variable)}.$$

* k = ratio of specific heat at constant pressure, divided by specific heat at constant volume.

It may be noted in passing that C_p is usually treated as a constant in the works of meteorologists, as by Margules in his paper, *Über die Energie der Stürme*, k. k. Centr.-Anst., Wien, 1903, where $n=1$ and R is a constant; or by v. Bjerknes in his *Dynamic Meteorology and Hydrography*, Carnegie Institution of Washington, 1910, Formula B, page 51, which gives

the value of $\frac{p}{p_0} = \left(\frac{T}{T_0}\right)^{\frac{1}{R\alpha} - 1} = \frac{n k}{k-1} - 1$, thus making $R=R_0$,

and the derivation of $\frac{p}{p_0}$, inconsistent with that of $\frac{P}{P_0}$, as may be seen by comparing (6), (7), (8). The system of units employed by v. Bjerknes makes $g=1$.

We have, therefore, adopted as the working formulas:

$$(6) \quad \frac{P}{P_0} = \left(\frac{T}{T_0}\right)^{\frac{k}{k-1}}. \quad \frac{P}{P_0} = \left(\frac{T}{T_0}\right)^{\frac{n k}{k-1}}.$$

$$(8) \quad \frac{\rho}{\rho_0} = \left(\frac{T}{T_0}\right)^{\frac{1}{k-1}}. \quad \frac{\rho}{\rho_0} = \left(\frac{T}{T_0}\right)^{\frac{n}{k-1}}.$$

$$(8)' \quad R = R_0. \quad \frac{R}{R_0} = \left(\frac{T}{T_0}\right)^{n-1}.$$

$$(9) \quad C_{p_0} = R_0 \frac{k}{k-1}. \quad C_p = R \frac{k}{k-1}.$$

It will be often convenient in making transformations to use the following auxiliary formulas. The mean values for T_1 and T_0 are expressed by \bar{T}_{10} , or for C_{p_1} and C_{p_0} by $C_{p_{10}}$.

$$(10) \quad n_1 C_{p_1} (T_1 - T_0) = C_{p_1} (T_1 - T_0)$$

$$(11) \quad n_1 C_{p_{10}} (T_1 - T_0) = C_{p_{10}} (T_1 - T_0)$$

$$(12) \quad C_{p_{10}} = R_{10} \frac{k}{k-1}.$$

$$(13) \quad \int \frac{dT}{T} = \frac{T_1 - T_0}{\bar{T}_{10}} = \frac{1}{M} \log \frac{T_1}{T_0} = \frac{1}{M} (\log T_1 - \log T_0).$$

$$(14) \quad \int \frac{dT_1}{T_1} = \frac{T_1 - T_0}{\bar{T}_{10}} = \frac{1}{M} \log \frac{T_1}{T_0} = \frac{1}{M} (\log T_1 - \log T_0).$$

$$(15) \quad \frac{T_1 - T_0}{\bar{T}_{10}} = \frac{1}{(n-1)} \frac{1}{M} \log \frac{R_1}{R_0} = \frac{1}{n-1} \cdot \frac{1}{M} (\log R_1 - \log R_0).$$

The reduction of the adiabatic system to the nonadiabatic system through the ratio of the temperatures is,

$$(16) \quad \left(\frac{T}{T_0}\right)_{\text{adiab.}} = \left(\frac{P}{P_0}\right)_{\text{adiabatic.}} = \left(\frac{T}{T_0}\right)_{\text{nonadiab.}}$$

$1 - \frac{1}{n} \quad \frac{k-1}{k} - \frac{k-1}{nk} = \frac{k-1}{k} \left(1 - \frac{1}{n}\right)$

We may now differentiate equation (6) for the nonadiabatic formula, with P, T, n variables, and P_0, T_0, k constants, using the type for the unit mass,

$$u = y^x, \text{ and } \frac{du}{u} = \log y \cdot dx + x \frac{dy}{y},$$

the result being, as given in (35), (36), M. W. R., March, 1906,

$$(17) \quad g dz = - \frac{dP}{\rho} + C_p T \log T dn \text{ (for nonadiabatic system).}$$

Since $g dz = - \frac{dP}{\rho}$ in the adiabatic system, it follows that

the term $+ C_p T \log T dn$ transforms the adiabatic into the nonadiabatic system. If a similar set of combinations, as for (1) (2) (3) to produce (4), be made with (17) (2) (3), we find,

$$(18) \quad \frac{dT}{T} = \frac{k-1}{nk} \frac{dP}{P} - \frac{C_p}{g} \alpha \log T dn,$$

which leads again to the difference between the two systems, as given in (16).

Circulation and radiation in the nonadiabatic system.

In the adiabatic system the fundamental relation is contained in the formula for no circulation, and no radiation of heat in the atmosphere,

$$(19) \quad g dz = - C_{p_0} dT = - \frac{dP_0}{\rho_0}.$$

If there is circulation we have by the differential general equation of motion,

$$(20) \quad g dz = - \frac{dP}{\rho} - q dq.$$

If in addition there is radiation of heat, it is

$$(21) \quad g dz = - \frac{dP}{\rho} q dq - dQ. \quad \text{Integrating,}$$

$$(22) \quad g(z - z_0) = - \frac{P_1 - P_0}{\rho_{10}} - \frac{1}{2} (q_1^2 - q_0^2) - (Q_1 - Q_0).$$

Now by passing to the limits the equation (18) can be readily transformed into

$$(23) \quad g(z-z_0) = -\frac{P_1 - P_0}{\rho_{1,0}} - (Cp_1 - Cp_{1,0})(T_1 - T_0),$$

and hence it is found by (22) and (23) that

$$(24) \quad -\frac{1}{2}(q_1^2 - q_0^2) - (Q_1 - Q_0) = - (Cp_1 - Cp_{1,0})(T_1 - T_0),$$

so that the departure of the specific heat from the adiabatic value $(Cp_1 - Cp_{1,0})$ and the departure of the temperature from the adiabatic rate $(T_1 - T_0)$ depend upon the circulation and the radiation. Hence in the adiabatic atmosphere there is no circulation and no radiation, and these occur only in the non-adiabatic atmosphere. The one invariable term is the gravity $g(z-z_0)$, and it may be broken up into three parts; one for pressure $g(z_1-z_0)$, one for circulation $g(z_1-z_1)$, and one for radiation $g(z_1-z_1)$. The purpose is to compensate by mutual adjustments such variations as occur so that the sum on a given level shall always be the same $g(z-z_0)$. We have, therefore, a large number of expressions which can be briefly summarized in equivalent vertical columns.

	ADIABATIC.	NONADIABATIC.
	Gravity	Pressure Circulation and Radiation
(25)	$g(z-z_0)$	$= g(z_1-z_0) + g(z_1-z_1) + g(z_1-z_1).$
(26)	$\int g dz$	$= -\int \frac{dP}{\rho} - \int q dq - \int dQ.$
(27)	$-\int Cp_1 dT$	$= -\int \frac{dP}{\rho} + \int Cp T \log T dn.$
(28)	$g(z-z_0)$	$= -\frac{P_1 - P_0}{\rho_{1,0}} - \frac{1}{2}(q_1^2 - q_0^2) - (Q_1 - Q_0).$
(29)	$-Cp_1(T_1 - T_0)$	$= -Cp_{1,0}(T_1 - T_0) - (Cp_1 - Cp_{1,0})(T_1 - T_0).$
(30)	$-n_1 Cp_1(T_1 - T_0)$	$= -n_1 Cp_{1,0}(T_1 - T_0) - n_1(Cp_1 - Cp_{1,0})(T_1 - T_0).$
(31)	$-\frac{1}{M} Cp_1 T_0 \log \frac{T_1}{T_0}$	$= -\frac{1}{M} n_1 Cp_{1,0} T_0 \log \frac{T_1}{T_0} - (Cp_1 - Cp_{1,0})(T_1 - T_0).$

It has been found by experience with the observed data in the free atmosphere that the terms in (26), (27), (28) do not balance, if one omits the radiation term $(Q_1 - Q_0)$. The gravity, pressure, and circulation as computed from the observations in cyclones, anticyclones, and in the general circulation, do not conform, and all the efforts of meteorologists to make them do so have been failures, or fictitious and improper solutions. The

$(Q_1 - Q_0)$ term is a large one, especially in the higher strata, as will be seen from the accompanying examples, and this cannot ever be computed with a constant specific heat C_p and gas coefficient R . At present there seems to be no method of computing $(Q_1 - Q_0)$ independently of $\frac{1}{2}(q_1^2 - q_0^2)$, but as the circulation can be determined by observations of the velocity in the different strata, we have,

$$(32) \quad (Q_1 - Q_0) = (C_{p_1} - C_{p_0}) (T_1 - T_0) - \frac{1}{2} (q_1^2 - q_0^2).$$

It also follows that observations which contain the height z , the pressure P , and the temperature T , but omit the velocity of circulation and the direction of motion q , are useless in problems of dynamic meteorology. If, furthermore, the relative humidity is omitted, there is no way of studying the constituents of the radiation $(Q_1 - Q_0)$, and the parts depending upon dry air and aqueous vapor respectively.

*Entropy, Work, Inner Energy, Radiation Function,
and Exponent of Radiation.*

Having derived the values of $(Q_1 - Q_0)$ through computations based upon observations, we can proceed to compute the fundamental thermodynamic terms applicable to a nonadiabatic atmosphere by the following formulas, where v is volume of unit mass, C_v and C_p are the specific heats of air at constant volume and constant pressure.

Entropy.

$$(33) \quad S_1 - S_0 = \frac{Q_1 - Q_0}{T_{10}} = n_1 C_p \frac{1}{M} \log \frac{T_1}{T_0} - \frac{1}{M} R_{10} \log \frac{P_1}{P_0} \\ = n_1 C_p \frac{(T_1 - T_0)}{T_{10}} - \frac{1}{M} R_{10} \log \frac{P_1}{P_0}.$$

External Work.

$$(34) \quad W_1 - W_0 = P_{10} (v_1 - v_0) = R_{10} (T_1 - T_0) - \frac{P_1 - P_0}{\rho_{10}} \\ = C_{p_{10}} \frac{k-1}{k} (T_1 - T_0) - \frac{P_1 - P_0}{\rho_{10}} = \left(\frac{k-1}{k} - 1 \right) \frac{P_1 - P_0}{\rho_{10}}.$$

Internal Energy.

$$(35) \quad U_1 - U_0 = C_{v_{10}} (T_1 - T_0) = (C_{p_1} - R_{10}) (T_1 - T_0) = \\ (C_{p_1} - C_{p_{10}} \frac{k-1}{k}) (T_1 - T_0) = C_{p_1} (T_1 - T_0) - \frac{k-1}{k} \frac{P_1 - P_0}{\rho_{10}}.$$

Heat Energy.

$$(36) \quad Q_1 - Q_0 = C_{v_{10}} (T_1 - T_0) + P_{10} (v_1 - v_0) = T_{10} (S_1 - S_0) \\ = (C_{p_1} - C_{p_{10}}) (T_1 - T_0) = C_{p_1} (T_1 - T_0) - \frac{P_1 - P_0}{\rho_{10}}.$$

Radiation Function.

$$(37) \quad K_{10} = \frac{U_1 - U_0}{v_1 - v_0} = \frac{Q_1 - Q_0}{v_1 - v_0} - P_{10} = \frac{T_{10} (S_1 - S_0)}{v_1 - v_0} - P_{10} \\ = \frac{R_a}{R_{10}} \cdot P_{10}.$$

Exponent of the radiating function.

$$(38) \quad \frac{K_1}{K_0} = \left(\frac{T_1}{T_0} \right)^A, \quad A = \frac{\log K_1 - \log K_0}{\log T_1 - \log T_0}.$$

It should be stated that the utmost care must be taken in the computations to use the exact quantities indicated in the formulas, and that having done so the numerous check computations are always fulfilled. Thus, there are three principal checks:

- (1) The Boyle-Gay Lussac Law, $P = \rho RT$,
- (2) The gravity, $g(z - z_0) = -\frac{P_1 - P_0}{\rho_{10}} - \frac{1}{2}(q_1^2 - q_0^2) - (Q_1 - Q_0)$,
- (3) The heat, $Q_1 - Q_0 = (W_1 - W_0) + (U_1 - U_0)$,

and these can be applied at the three important stages of the computing.

Application of the Formulas to Meteorological Data.

The following balloon ascensions have been computed by this method, and a brief summary of the results is added for discussion:

Lindenburg, . . . April 27, 1909, latitude $+52^\circ$ by Assman.

May 5, 1909,

May 6, 1909,

July 27, 1908,

Sept. 2, 1909,

Mailand, Sept. 7, 1906, latitude $+45^\circ$ by Berson and Coyne.

Atlantic Ocean, Sept. 25, 1907, latitude $+35^\circ$ by Teisserenc de Bort and Rotch.

Sept. 9, 1907, " $+25^\circ$.

Aug. 29, 1907, " $+13^\circ$.

July 29, 1907, " $+13^\circ$.

June 19, 1906, " -2° .

Victoria Nyanza, Aug. 30, Sept. 5, 1908, latitude 0° by Berson.

TABLE I.

Lindenburg Balloon Ascension, April 27, 1909.

Computations for the data relating to circulation and radiation.

z Eleva- tion in meters	T Tempe- rature	n $n = \frac{a_s}{a}$	P Pres- sure	ρ Density	R Gas coeff- cient	C_{p10} Specific heat	$\frac{p_1}{p_2} - \frac{p_1}{p_2}$	$\frac{p_1}{p_2} - \frac{p_1}{p_2}$	$\frac{p_1}{p_2} - \frac{p_1}{p_2}$	Diff.
Check formula (1)						Check formula (2)				
18000	202.7	12.837	16464	0.8276	247.92	877.79	8650.8	+ 29.8	1118.0	+ 13.4
12000	208.5	1.5421	19478	0.8692	259.25	904.98	8929.2	- 24.9	899.3	+ 2.4
11000	209.9	1.1215	22980	0.4153	268.68	914.86	9025.4	- 42.3	819.2	+ 3.7
10000	218.7	0.9969	26958	0.4651	264.95	917.08	9046.2	- 24.2	779.2	+ 4.6
9000	228.6	0.8294	31402	0.5185	264.92	913.07	9008.6	- 2.2	796.8	+ 2.8
8000	240.5	1.1215	36328	0.5751	262.64	911.11	8983.6	+ 30.9	788.0	+ 8.5
7000	249.8	1.4099	41764	0.6351	263.79	918.31	9082.2	+ 72.9	670.0	- 19.1
6000	256.8	1.4954	47809	0.6992	266.79	929.38	9165.6	+ 26.3	607.4	+ 6.7
5000	262.9	1.5919	54582	0.7678	270.18	941.73	9289.0	- 108.2	619.9	+ 5.3
4000	269.1	1.4954	62004	0.8411	273.93	953.95	9418.5	- 50.9	442.0	- 8.6
3000	275.7	1.6449	70296	0.9197	277.24	963.04	4750.6	- 46.9	197.6	+ 1.7
2500	278.7	2.1455	74768	0.9609	279.18	970.98	4792.2	- 43.6	155.2	- 0.8
2000	281.0	2.1455	79470	1.0085	281.82	980.14	4894.2	- 25.0	91.3	+ 2.5
1500	283.8	1.5421	84428	1.0476	284.46	987.72	4867.4	+ 5.3	23.6	+ 6.7
1000	286.5	1.3707	89633	1.0932	286.21	993.02	4904.2	+ 8.2	- 5.4	- 4.0
500	290.1	0.8814	95115	1.1403	287.53	994.45	3768.5	- 57.5	54.3	+ 0.2
116	294.4	—	99482	1.1778	287.08	—	—	—	—	—
						$g(z-z_0)$ $(z-z_0)$	3765.5 884	4903.0 500	9806.0 1000	

Check formula (3)

z	$Q_1 - Q_0$	T_{10}	$S_1 - S_0$	$\frac{R_{10}}{(T_{10} - T_0)}$	$W_1 - W_0$	$U_1 - U_0$	$v_1 - v_0$	K_{10}	A
18000	- 1118.0	203.10	- 5.480	- 2511.4	+ 6189.4	- 7252.4	0.8440	- 21082	3.45
12000	- 899.8	206.70	- 4.851	- 2573.1	+ 6356.1	- 7255.4	0.8004	- 24152	4.86
11000	- 819.2	214.30	- 3.823	- 2596.4	+ 6429.0	- 7248.2	0.2582	- 28072	3.64
10000	- 779.2	223.60	- 3.485	- 2607.8	+ 6488.4	- 7217.6	0.2214	- 32800	3.44
9000	- 796.8	234.60	- 3.896	- 2602.7	+ 6405.9	- 7202.7	0.1897	- 37968	2.73
8000	- 788.0	244.90	- 3.197	- 2606.6	+ 6377.0	- 7160.0	0.1642	- 43605	3.11
7000	- 670.0	252.80	- 2.650	- 2716.3	+ 6365.9	- 7035.9	0.1443	- 48751	4.79
6000	- 607.4	259.60	- 2.340	- 2657.4	+ 6508.2	- 7115.6	0.1278	- 55677	5.40
5000	- 619.9	266.00	- 2.330	- 2653.7	+ 6635.3	- 7255.2	0.1186	- 63866	4.24
4000	- 442.0	272.40	- 1.623	- 2705.1	+ 6713.4	- 7155.4	0.1015	- 70495	3.63
3000	- 197.6	277.20	- 0.713	- 1359.4	+ 3391.2	- 3588.8	0.0466	- 76977	4.89
2500	- 155.2	279.85	- 0.555	- 1371.6	+ 3420.6	- 3575.8	0.0443	- 80720	5.10
2000	- 91.3	282.15	- 0.824	- 1890.1	+ 3444.1	- 3585.4	0.0420	- 84176	4.71
1500	- 23.6	284.90	- 0.083	- 1409.6	+ 3457.8	- 3481.4	0.0398	- 87472	5.54
1000	+ 5.4	288.30	+ 0.018	- 1389.5	+ 3514.7	- 3509.8	0.0377	- 93085	5.44
500	- 54.3	292.25	- 0.186	- 1072.1	+ 2696.4	- 2750.7	0.0276	- 99640	
116	—	—	—	—	—	—	—	—	

The values of the contents in the formulas are all taken from Table 14,
M. K. S. System, Monthly Weather Review, March, 1906.

The ascension of April 27, 1909, is given separately in order to show more fully the scope of the computing, in Table 1, and the summary in Table 2 is arranged to bring out the relations in the Middle Latitudes and in the Tropics. The data for Victoria Nyanza are taken from the Meteorol. Zeit., Dec., 1910, which is a mean of several ascensions, especially Aug. 30 and Sept. 5, 1909. Above the 17,000 meter level the temperature of Aug. 30, lower than -75°C. , should be verified for several reasons before accepting them as characteristic of the strata at the elevation 17 to 19 kil. over the equator.

The observed temperature at the given height is the basis of the reduction, the value of n being found by taking the adiabatic gradient for the difference of elevation and dividing it by the observed difference. It varies from the adiabatic system at all strata, and it may become very large, having positive or negative values in nearly isothermal layers. The value of n is assumed to be uniform in the stratum from which it is computed by the top and bottom temperatures. The check $P = \rho RT$ is complete throughout. The pressure being reduced to meters of mercury agrees closely with that observed. The gas coefficient and the specific heat are variables characteristic of nonadiabatic atmospheres. Since the adiabatic specific heat is $C_{p_a} = 993.58$ it is seen that $(C_{p_a} - C_{p_i}) (T_a - T_i)$ becomes a very large quantity, especially in the upper strata, and it is equal to $\frac{1}{2}(q_i^2 - q_a^2) + (Q_i - Q_a)$ the kinetic energy of circulation and of heat radiation between the two levels. The second check equation is closely fulfilled, but the small differences indicate that the data of the temperatures are not perfectly adjusted to the elevation. It should be especially noted that the equation in common use by meteorologists,

$$g(z - z_0) = - \frac{P_1 - P_0}{\rho_{10}} \frac{1}{2} - (q_i^2 - q_a^2)$$

is unbalanced, lacking the large heat term $(Q_i - Q_a)$, and on that account the ordinary dynamic data are never adjustable without the compensation for the loss of heat by radiation. It is seen that the entropy increases with the height if the temperature steadily diminishes, but changes from negative to positive values in cases of an inversion, as in the stratum 500 to 1000 meters. The third check equation $(Q_i - Q_a) = (W_i - W_a) + (U_i - U_a)$ is confirmed, and the escaping heat depends upon an excess in the loss of the inner energy over the external work. The loss of the inner energy is nearly constant per 1000 meters, $U_i - U_a = 7152$, but the work diminishes with the altitude and the decrease of the density, so that $Q_i - Q_a$, the loss of heat, increases with the elevation, whose rate of change will be further noted. The radiating function,

$$K = \frac{U_1 - U_0}{v_1 - v_0},$$

is readily computed from the inner energy and the density, since $v = \frac{1}{\rho}$, and the volume increases with the elevation.

Finally, the exponent of radiation

$$\frac{K_1}{K_0} = \left(\frac{T_1}{T_0} \right)^A,$$

can be computed from the K and T columns, and the result is to show that the value of A is substantially 4.00, so that the air radiates like a full black body, according to the Stefan Law. It seems to be somewhat larger than 4.00 in the lower levels and in the isothermal layer, and a little less than 4.00 in the layers below the isothermal layer, as will be further indicated. A similar study of these thermodynamic data in the diurnal convection near the surface, and in the cyclones and the anticyclones, contains many points of interest that must be discussed in other papers.

The Mean Data for Europe, the North Atlantic Tropics, and Victoria Nyanza.

In Table 2 we collect the mean values of the data as computed, five ascensions at Lindenburg, lat. $+52^\circ$, one at Milan, lat. 45° , five on the Atlantic Ocean from latitude $+35^\circ$ to -2° , and two at Victoria Nyanza, lat. 0° . The variations in each group, due to local conditions, are fairly well eliminated, but a much larger series of computations would be desirable. The temperature T seems to indicate an excess of degrees in the high pressure belt from $z = 2000$ to $z = 10,000$, as shown in my paper, Mt. Weather Bulletin, vol. 3, part 3, 1910.

The isothermal layer sets in at 13,000 m. in Europe, 15,000 m. in the Tropics, and was not reported as reached at Victoria Nyanza. The gradients average -6.4 for Europe in summer, -6.0 in the Tropics, -6.3 over East Africa. The gradient ratio n is positive in all levels except where there is an inversion of temperature, as shown in the isothermal levels. The means here given in this layer were found by omitting from the summation several of the results which are excessive, and

due to a small denominator in $n = \frac{T_1 - T_0}{T_1 - T_0}$, where $T_1 - T_0$ is

often only 0.1° or 0.2° ; for $T_1 = T_0$, $n = \alpha$. The average value of n is 2.0 in the levels 000 to 5000 m., 1.5 in the levels

TABLE 2.
Temperature T Gradient Ratio n

2 in meters	Europe	Atlantic Ocean	Victoria Nyanza	Europe	Atlantic Ocean	Victoria Nyanza
18000	222.6	—	190.5 *	-2.170	-2.117	1.495
17	219.5	227.0	197.1 †	-7.676	-3.126	1.795
16	223.4	217.3	202.6	-4.423	-0.940	2.350
15000	221.2	209.9	206.8	-6.580	0.626	2.467
14	220.3	212.8	210.8	-5.059	2.425	1.898
13	215.7	215.9	216.0	-0.963	1.744	1.495
12	215.8	221.6	222.6	1.370	1.207	1.122
11	218.7	230.3	231.4	1.188	1.156	1.316
10000	226.0	238.9	238.9	1.155	1.124	1.371
9	232.8	247.7	246.1	1.545	1.387	2.146
8	241.1	254.9	250.7	1.270	1.397	1.352
7	249.0	260.1	258.0	1.437	1.604	1.828
6	256.1	268.3	263.4	1.598	1.774	1.702
5000	262.6	274.1	269.2	1.779	2.262	1.795
4	268.3	278.5	274.7	1.591	1.962	1.618
3	274.3	283.9	280.8	2.488	1.734	1.299
2	279.1	288.8	288.4	1.976	3.298	1.265
1	284.8	292.4	296.2	2.512	1.386	—
000	289.4	299.5	—	—	—	—

Pressure P				Density ρ		
18000	7851	—	7816	0.1949	—	0.1856
17	9141	9894	9324	0.2220	0.2256	0.2104
16	10983	11213	11063	0.2476	0.2513	0.2375
15000	12819	13381	13071	0.2764	0.2788	0.2675
14	14972	15665	15394	0.3086	0.3128	0.3005
13	17017	18398	18066	0.3422	0.3502	0.3367
12	19042	21442	21114	0.3830	0.3911	0.3762
11	23341	24942	24548	0.4283	0.4355	0.4187
10000	27198	28853	28383	0.4780	0.4830	0.4643
9	31606	33204	32675	0.5315	0.5338	0.5132
8	36509	38038	37490	0.5890	0.5879	0.5659
7	41973	43413	42883	0.6504	0.6459	0.6226
6	48053	49879	48890	0.7162	0.7079	0.6834
5000	54819	56008	55582	0.7865	0.7742	0.7487
4	62353	63330	63020	0.8620	0.8453	0.8187
3	70722	71569	71370	0.9429	0.9217	0.8935
2	80030	80625	80364	1.0299	1.0031	0.9731
1	90345	90699	88870	1.1224	1.0908	1.0453
000	100419	101753	—	1.2101	1.1837	—

Specific Heat Cp				Velocity q (m.p.s.)		
18000	624.41	—	765.38	1.9	—	14.9
17	657.15	668.93	778.43	0.8	8.0	13.6
16	689.35	709.00	795.63	2.5	7.4	10.7
15000	731.44	738.87	817.98	3.9	8.3	7.8
14	769.99	814.91	841.30	3.6	8.5	9.3
13	799.60	835.84	859.90	14.3	14.3	8.9
12	836.65	855.58	872.84	16.4	13.8	6.5
11	863.20	861.08	876.94	17.8	13.3	8.6
10000	873.16	865.62	885.82	19.3	12.4	7.2
9	884.82	869.26	895.64	20.7	12.0	5.2
8	890.49	878.51	914.82	18.4	11.8	6.0
7	897.75	887.63	924.12	16.3	10.7	5.8
6	907.35	899.98	940.12	12.6	9.9	4.5
5000	919.62	913.55	954.60	14.1	6.6	6.0
4	934.08	931.88	970.06	13.0	6.5	4.4
3	947.41	946.73	983.32	12.6	6.5	3.1
2	964.88	963.44	991.20	11.6	5.8	4.5
1	979.50	984.35	991.58	9.2	4.4	3.1
000	993.58	993.58	—	6.1	5.8	—

* Height of Victoria Nyanza, 1140 meters.

† Height of Lindenburg, 116 meters.

TABLE 2—continued.
Heat Expended (Q_1-Q_0) Entropy (S_1-S_0)

2 in meters	Europe	Atlantic Ocean	Victoria Nyanza	Europe	Atlantic Ocean	Victoria Nyanza
18000	-3459	—	-2206	-15·596	-14·816	-11·385
17	-3231	-8013	-2074	-14·747	-13·359	-10·376
16	-2791	-2570	-1870	-12·620	-10·292	-9·186
15000	-2392	-1898	-1605	-11·158	-8·567	-7·688
14	-1955	-1584	-1415	-8·068	-7·361	-6·629
13	-1702	-1470	-1274	-7·487	-6·697	-5·809
12	-1381	-1345	-1156	-6·826	-5·949	-5·091
11	-1190	-1302	-1118	-5·845	-5·545	-4·756
10000	-1089	-1250	-1028	-4·722	-5·185	-4·287
9	-1131	-1182	-868	-4·768	-4·699	-3·493
8	-1034	-1100	-783	-4·229	-4·252	-2·880
7	-920	-1000	-618	-3·647	-3·769	-2·352
6	-793	-881	-448	-3·083	-3·247	-1·684
5000	-650	-700	-317	-2·578	-2·584	-1·165
4	-580	-532	-172	-1·957	-1·907	-0·618
3	-380	-397	-57	-1·375	-1·888	-0·201
2	-241	-187	-8	-0·857	-0·641	-0·083
1	-77	-24	—	-0·241	-0·081	—
000	—	—	—	—	—	—

Work (W_1-W_0)			Inner Energy (U_1-U_0)		
18000	4815	—	5421	-8274	—
17	4658	4911	5525	-7887	-7922
16	4962	5203	5664	-7758	-7774
15000	5209	5609	5811	-7602	-7506
14	5540	5750	5956	-7494	-7384
13	5730	5911	6087	-7431	-7381
12	5948	6024	6130	-7329	-7369
11	6096	6060	6188	-7285	-7362
10000	6164	6086	6245	-7253	-7336
9	6248	6127	6341	-7379	-7309
8	6302	6199	6455	-7336	-7298
7	6329	6271	6544	-7249	-7271
6	6405	6368	6643	-7198	-7248
5000	6510	6473	6750	-7160	-7173
4	6601	6591	6853	-7131	-7123
3	6717	6694	6930	-7097	-7091
2	6825	6846	6974	-7066	-7033
1	6969	6911	—	-7045	-6935
000	—	—	—	—	—

Radiation Energy K_1			Exponent of Radiation A		
18000	14844	—	12005	—	4·44
17	16704	17488	13968	—	4·92
16	16497	16647	15908	—	5·92
15000	20083	19328	18060	—	6·82
14	21850	21544	20582	—	5·66
13	23888	24731	23624	3·86	5·37
12	26548	28286	27013	5·13	3·90
11	29953	32588	31143	8·87	3·70
10000	34502	37288	35422	4·13	3·56
9	40630	42938	39717	3·78	4·25
8	45275	47822	44616	3·98	4·41
7	51345	53935	50082	4·25	4·33
6	57729	59582	55577	4·60	5·10
5000	64352	65980	61930	5·19	5·76
4	71739	72304	68663	3·66	4·63
3	77430	78606	74258	5·94	4·55
2	86011	86055	82802	5·24	5·64
1	94582	98056	—	6·09	5·21
000	—	—	—	—	—

6000 to the isothermal layer, and then becomes negative and probably of increasing amounts. The tendency to negative values sets in high over the equator and then diminishes in elevation towards the poles.

The pressure P is higher over the middle Tropics (latitude 20°) than over the equator or over Europe, and shows the high pressure belt to the level 17,000 meters. The barometric pressure is $B = P/g\rho_m$, where $\rho_m = 13595.8$ the density of mercury in kilograms per cubic meter, and $g = 9.8060$ the acceleration of gravity in meters per second. At Lindenburg the pressure difference between computed and observed values shows that the observed values range from 0^{mm} to 1.5^{mm} larger in the strata up to the highest altitude reached; the observations in the Tropics are more nearly accordant, the observed pressures being 0.0^{mm} to 0.5^{mm} smaller than the computed. The pressure over Europe is less than over the Tropics in all levels, and hence there is an eastward wind movement over Europe, and a westward movement over the Tropics between the high pressure belt and the equator. The density ρ increases from the equator to the poles up to 10,000 meters, and about that level becomes higher over the middle Tropics than to the north or south.

The specific heat C_p is a variable ranging from 993 to 624 in these computations. This departure from the normal value 993 increases with the height, and by the formula,

$$(C_{p_s} - C_{p_n})(T_s - T_n) = \frac{1}{2}(q_s' - q_n') + (Q_s - Q_n),$$

is responsible for the kinetic energy of circulation per unit mass and that of radiation. Since $\frac{1}{2}(q_s' - q_n')$ depends upon the change of the velocity per 1000 meters, and since the velocities are small in the isothermal layer, it follows that the loss of heat $(Q_s - Q_n)$ is due to the change in the specific heat at high elevations together with the low pressure and density dependent upon the observed temperatures. The complex thermodynamic adjustment involved in the formulas cannot be easily summarized in a sentence, but it will become clearer to the reader by considering the following paragraphs. The specific heat on the East African plateau was assumed to be 993 at the surface, though the elevation is 1140 meters above sea level, and so the computed C_p is not readily compared in the upper levels with the data of the Tropics and Europe. It is probably about the same in the free air at all levels in all latitudes, when the plateau effect has been eliminated.

The velocity q increases from the ground up to the isothermal layer, and then rather suddenly drops in amount in this layer. The velocity generally increases from the Tropics towards the poles, including latitude 52° , as is well known.

The expended heat ($Q_1 - Q_0$) per 1000 meters in elevation increases in amount by two distinct systems, one in the strata from the surface to the isothermal layer, and another in that layer. Take the differences in the columns for ($Q_1 - Q_0$) of Table 2, and these are found in Table 3.

TABLE 3.

The variation in the loss of heat per 1000 meters.

$$\frac{d}{dz} \frac{dQ}{dz} = \frac{d}{dz} (Q_1 - Q_0) = \text{Constants.}$$

Height z	Europe	Tropics	Victoria Nyanza
18000	-228	—	-132
17	-440	-442	-204
16	-399 -346	-672* -378	-265
15000	-437	-314	-190
14	-253	-114	-141
13	-321	-125	-118
12	-211	-43*	-38*
11	-101	-52*	-90
10000	+ 42*	-68*	-160 -143
9	-97	-82	-135
8	-114	-100 -140	-120
7	-127 -137	-119	-165
6	-143	-181	-131
5000	-120	-168	-145
4	-150	-135	-115
3	-139	-210	-49
2	-164	-163	-8
1	-77	-24	—
000	—	—	—

$$\text{Mean } \frac{\Delta(Q_1 - Q_0)}{1000} = -362 \text{ for the isothermal layer.}$$

$$\text{Mean } \frac{\Delta(Q_1 - Q_0)}{1000} = -140 \text{ for the lower layers.}$$

There are three facts to be noted, (1) that from the surface to about 2000 meters, in the stratum within which the diurnal convection is confined, the loss of heat diminishes less than in the strata above 2000 meters. In the lower levels there is an accession of heat which prevents as rapid cooling as in the higher levels, and this is probably due to the condensation of the aqueous vapor, which is a source of heat in addition to that

radiated from the surface. The incoming radiation, after certain depletions by scattering and absorption in the atmosphere generally, raises the surface of the ground or water to a certain temperature which radiates with long waves. The outgoing radiation passes through three stages:

(1). In the levels 000 to 2000 meters, where the heat supply is due to radiation at surface temperatures and the heat of condensation of aqueous vapor.

(2). In the levels 2000 meters to the isothermal layer, where the radiation is chiefly from the dry air, and there is no additional supply of heat of importance from the condensation. The constant of accelerating loss is about -140 .

(3). In the isothermal layer the radiation is much more rapid, with a constant acceleration of loss of about -362 , in spite of the fact that the temperature itself is nearly constant or slightly higher than at the lower boundary of the isothermal region. In Europe the isothermal temperatures are about 202° to 208° , and in the Tropics about 209° , generally, not counting the single observation at Victoria Nyanza.

It should be noted, in passing, that the thermodynamic data give no support to Abbot's hypothesis of an effective radiation layer at 5000 meters, since the only disturbance in these values is just below and on entering the isothermal layer. The various hypotheses regarding the origin of the heat found in this layer may properly be revised. There is apparently a congested or mixing region on the north side of the high pressure belt, in the temperate latitudes at lower levels, 10,000 to 13,000 meters, and over the tropics at higher levels, 13,000 to 15,000 meters, and this may be in part due to some form of overflow during the general process of polar circulation. The theory that it is due to such by-products of the incoming radiation as ozone formation is contradicted by the fact that such formation should be able to penetrate to lower levels over the Tropics than over the temperate zones, which is contrary to the entire series of facts. In my opinion the apparent heat of the isothermal layer is due to the inability of the radiation to escape fast enough to reach the thermodynamic demands implied in

$$(C_{p_a} - C_{p_{10}}) (T_a - T_{10}),$$

although it is observed to carry off heat in the isothermal layer much more rapidly than in the lower levels. That is to say, $(C_{p_a} - C_{p_{10}})$ increases so rapidly with the elevation that $(T_a - T_{10})$, the departure of the temperature from stratum to stratum upon which $C_{p_{10}}$ depends, cannot proceed rapidly enough by means of radiation losses to give the temperature fall observed in the lower strata. This choking process sets in at a certain low temperature, 202° to 208° , and of course the

primary physical question becomes the natural rate of radiation of heat at certain low temperature wave lengths. In any event the marked change in the loss of heat, from -140 to -362 per 1000 meters below and within the isothermal layer, is involved in the physical conditions of the phenomena. Before crossing the boundary of the isothermal layer there is an increase in the heat supply, as at the values marked with a cross and omitted from the summation, as if there was a congestion or accumulation of heat, in the cirrus cloud region, before changing from the slow rate of loss -140 to the rapid loss -362 . It is apparent that further studies of these data are likely to lead to a differential equation of radiation, which differs from the theoretical equations that have been hypothetically proposed by several authors.

The Entropy ($S_1 - S_0$) increases with the height, but more rapidly on entering the isothermal layer; it increases generally from the equator towards the poles, except in the high pressure belt, from 3000 to 8000 meters elevation.

The work expended ($W_1 - W_0$) diminishes with the height, and more rapidly towards the temperate zone except in the same region of the high pressure belt.

The inner energy ($U_1 - U_0$) is substantially a constant, about 7200 per 1000 meters, except in the strata near the surface where it is smaller 7000, and in the isothermal layer where it is larger and increasing to 8000 or more.

The radiation energy $K_{1,0} = \frac{U_1 - U_0}{v_1 - v_0}$ is of course similarly distributed and ranges from 94,000 near the surface to 13,000 at the 18,000 meter level. The loss of radiant energy is accomplished by means of the complex thermodynamic processes just described, and it is quite unavailing to discuss this problem by means of generalized simple equations that take no account of the mechanical and thermal requirements of the atmosphere.

The exponent of radiation $A = \frac{\log K_1 - \log K_0}{\log T_1 - \log T_0}$ is about 4.00 in value, and the atmosphere conforms to the radiation of a black body. In the lower levels this exponent is larger, probably due to the heat contents of the condensing aqueous vapor. This can be separated from the dry air as follows:

$$\frac{K_1}{K_0} = \left(\frac{T_1}{T_0} \right)^A = \left(\frac{T_1}{T_0} \right)^{4.00 + (A - 4.00)} = \left(\frac{T_1}{T_0} \right)^{4.00} \times \left(\frac{T_1}{T_0} \right)^{A - 4.00}$$

dry air vapor

Thus if $A = 5.50$,

$$\frac{K_1}{K_0} = \left(\frac{T_1}{T_0} \right)^{4.00} \times \left(\frac{T_1}{T_0} \right)^{1.50}$$

dry air vapor

TABLE 4. The exponent of A in $\frac{K_1}{K_0} = \left(\frac{T_1}{T_0} \right)^A$ on entering the isothermal layer.

Z Height Lat.	May 5 1909 52°	July 27 1908 52°	Sept. 2 1909 52°	Sept. 7 1906 45°	Sept. 25 1907 35°	Sept. 9 1907 25°	Aug. 29 1907 19°	July 29 1907 18°	June 19 1906 -2°	Vic. Nya. 1908 0°
18000	- 1.53	- 8.06	+ 18.35	----	----	- 5.02	----	----	----	4.44
17	+ 3.50	- 43.30	----	----	- 8.07	- 1.82	----	----	----	4.92
16	- 10.34	- 12.72	----	- 2.63	- 175.80	- 1.11	+ 33.77	+ 37.81	----	5.92
15000	- 21.11	- 101.54	----	- 4.74	- 110.87	- 5.17	5.21	4.23	3.63	6.82
14	- 5.78	- 11.43	- 88.66	- 14.33	+ 117.05	+ 13.90	5.86	6.97	3.26	5.66
13	- 3.41	- 5.53	+ 11.39	+ 4.27	+ 145.08	+ 6.92	4.09	3.46	7.00	4.45
12	+ 13.29	+ 6.41	+ 54.76	4.11	+ 3.86	4.03	4.07	4.78	2.78	3.67
11	4.40	3.63	- 68.05	2.84	3.62	3.08	3.78	4.09	3.93	4.03
10000	4.97	4.05	- 19.59	4.21	3.28	3.73	3.75	3.01	4.03	3.86
9	0.71*	3.68	4.60	4.35	4.32	3.49	4.01	4.86	4.56	6.28
8	5.15	3.51	3.43	4.85	4.07	4.67	5.68	3.37	4.28	4.02
7	3.95	4.74	3.26	5.18	4.58	5.06	2.67	4.72	4.62	5.02
6	3.89	4.57	7.18	2.66	- 3.36	3.52	5.25	6.08	5.56	4.97
5000	6.48	4.07	4.25	6.18	5.51	6.98	6.27	5.38	4.68	5.10
4	3.63	4.00	2.70	2.55	5.34	2.78	3.82	4.34	6.88	3.57
3	7.24	4.50	6.90	6.33	5.52	4.59	4.13	3.35	5.15	4.08
2	8.73	3.89	4.06	4.17	7.87	5.12	4.52	4.63	6.07	3.94
1	- 8.29*	26.93*	6.74	18.68	4.64	- 46.40	3.41	8.23	4.55	----
000	----	----	----	----	----	----	----	----	----	----

The ascensions of April 27 and May 6, only reaching 18,000 meters, are here omitted.

Further studies on this subject have been undertaken. Table 4 gives an exhibit of the values of A for ten ascensions, for the purpose of showing the turbulent nature of this exponent near the surface of the earth, and especially in the isothermal layer. Near the equator the computed values of A are approximately 4.00 to great altitudes, but they become very large and unsteady in the isothermal layer, in a region which increases in latitude as it descends in altitude. This is due to the fact that,

$$n = \frac{T_1 - T_0}{T_1 - T_0},$$

where T_1 is nearly the same as T_0 , that is, the temperature is nearly equal in the layer of computation. It is through such irregularities that the formulas are compelled to proceed in computing P , ρ , R and the other terms from the observed T in the nonadiabatic atmosphere, and this shows how impossible it is to expect to successfully apply the adiabatic formulas, for $n=1$ and R , C_p constant, in these meteorological problems.

Transformation of the heat units. The K. M. S. system of units is transformed to the C. G. S. system by the factor $1000 \times 100 \times 100 = 10^8$. The mechanical equivalent of heat in the K. M. S. system is 4185.57 kilogram-meters or 4.18557×10^{10} C. G. S. for 1000 meters in the stratum. For example, having 660 mechanical units K. M. S. per 1000 meters; this is equivalent to 0.1577 large calories or 157.7 small calories per 1000, or 0.1577 small calory per' meter of altitude per square meter of surface. In this way the mechanical units of heat $Q_1 - Q_0$ (K. M. S.) in Table 2 can be converted into small calories per square meter and then submitted to an integration.

Conclusion.

(1) The dry air radiates like a perfect black radiator with the Stefan exponent 4.00 from the level 2000 meters to the isothermal layer. In the surface stratum it is more than 4.00, due to the added heat of condensing aqueous vapor, and in the isothermal layer it is very irregular, due to the small changes in the value of the temperature per 1000 meters.

(2) The isothermal layer of relatively high temperature seems to be due to a congestion in the rate of radiation, depending upon the complex thermodynamic relations of the pressure, density, gravity, which produce a large change in the specific heat, a small change in the temperature, but an accelerated loss of radiant heat.

ART. XLVI.—*Note on Atmospheric Radiation*; by FRANK W. VERY.

THE heat which gives to any layer of the atmosphere its observed temperature is derived from several sources which may be designated as follows:

- + h_c = heat transferred by convection from warmer and lower layers of air.
- + h_p = heat transferred by molecular penetration from warmer neighboring air masses in any direction.
- + h_w = heat derived from the condensation of aqueous vapor.
- + h_s = heat from absorption of solar radiation by the molecules of gases and vapors, or by floating dust from which it is transferred to gaseous molecules.
- + h_t = heat from a similar absorption of terrestrial radiation.
- + h_a = heat produced by absorption of radiation from warmer air masses, situated either above or below, but usually below. Here each atmospheric ingredient absorbs selectively and solely the radiations of those special wavelengths which it can itself emit.
- ± h_i = heat from chemical changes, such as ionization by solar ultra-violet radiation. The heat produced in this way may be included under the heat (h_s) from absorption of the sun's rays. The direct effect of ionization on temperature is probably small, but it may have important secondary consequences through the production of peculiar substances in small amount, but possessing extraordinary powers of selective radiant absorption and emission.
- ± h_q = heat imported, or abstracted by the planetary atmospheric circulation.

The relative importance of these sources of thermal supply varies greatly at different elevations. In the isothermal layer (3), the heat received is

$$H_s = h_c + h_a + h_p \pm h_q.$$

Convection may not have ceased entirely, but it is very small, and has been omitted from the expression. There are no clouds here and terrestrial radiation passes through unchanged, having suffered all the absorption of which it is capable in lower layers. The heat from absorption of solar rays becomes exceptionally powerful where the solar radiation first enters the aqueous atmosphere in the higher levels of the isothermal layer.

Between the isothermal layer and the air near the ground lies the great body of the cloud-producing atmosphere (2), where

$$H_s = h_c + h_p + h_w + h_s + h_t + h_i \pm h_q.$$

Near the earth's surface, the absorption of terrestrial radiation replaces that of the sun's rays to a great extent, because the absorbable part of the latter has already been removed by the upper air, except as the dust of the lower air absorbs radiation of every wave-length. The terrestrial radiation is chiefly effective in warming a shallow layer of air (1) near the ground, and its absorbable rays are soon sifted out in passing through the lower humid layers; but it is also efficient at any level where there is cloud and where the regions of absorption in the spectrum of terrestrial radiation are much broader. Emphasizing this importance of heat from absorption of terrestrial radiation by aqueous vapor, it is placed first on the list in the enumeration of heat sources for the superficial layers.

$$H_1 = h_1 + h_c + h_p + h_w + h_a + h_s \pm h_q.$$

The heat thus acquired may be removed by evaporation of precipitated water particles ($-h_c$), by atmospheric radiation ($-h_r$), by convection ($-h_c$) and by penetration ($-h_p$). If there is thermal equilibrium,

$$\begin{array}{ll} \text{at level} & (3), \quad h_1 + h_a + h_p \pm h_q - (h_r + h_{p_1}) = 0, \\ \text{"} & (2), \quad H_1 - (h_1 + h_r + h_c + h_{p_1}) = 0, \\ \text{"} & (1), \quad H_1 - (h_1 + h_r + h_c + h_{p_1}) = 0. \end{array}$$

Except in the upper air, the distance through which atmospheric radiation can proceed before it is reabsorbed by the air, is so small that convection and penetration might be expected to supersede radiation as available modes of thermal transference from one body of air to another. We are at last able to apply a critical test to this supposition.

The study of the vertical distribution of thermal losses in the earth's atmosphere which Professor Bigelow has made,* permits for the first time a comparison of atmospheric radiation, transferred from layer to layer in the free air, with that computed from laboratory measures.

The radiation from a layer of pure dry air, 1 meter in depth, and having an excess of temperature of 10°C. , may be taken as equivalent to a transference of 0.00006 gram-water-degree-Centigrade units of heat per second through each square centimeter of surface.† Bigelow divides the atmosphere into layers 1000 m. deep. The difference of temperature at the top and bottom of each layer is somewhat less than 10° , varying in fact between 5° and 7°C. throughout a considerable part of the first 10,000 meters. If radiation (R) from layer to layer is

* Frank H. Bigelow—"The Thermodynamics of the Earth's Non-adiabatic Atmosphere," this Journal, *xxiv*, 515-532.

† Frank W. Very—"Atmospheric Radiation." Bulletin G, U. S. Weather Bureau, p. 112, 1900.

simply proportional to the depth of the layers and to the fourth power of the absolute temperature, we get the values in the third column of the following table. This, however, in no case represents the *direct* radiation of the atmosphere from layer to layer, because the selective radiations of the gaseous molecules can proceed but a little way before they are absorbed by other molecules of the same gas. These in turn radiate again to cooler ones at a still higher level, and so on,* but the number of successive transferences of heat is very great even in a layer no more than one thousand meters thick, and the process is a slow one, not to be compared for rapidity with the rate of escape of unimpeded radiation.

Taking averages through the first 15,000 meters of air, we get the following mean values of energy expended as radiation in large calories per square meter, for comparison with Bigelow's ΔQ , or "heat expended."

Elevation	Per thousand meters		
	ΔT	R (computed)	ΔQ (observed)
Upper layer 15000—10000 ^m	0.96 C.	0.057	0.408
Middle layer 10000— 5000	7.3	0.429	0.237
Lower layer 5000— 0	5.4	0.314	0.090

The sudden diminution of the computed radiation (from stratum to stratum) in the upper layer follows from the entrance into the isothermal region, and from the diminution of ΔT ; but this does not imply a cessation of atmospheric radiation in this nonadiabatic layer. On the contrary, the observed increase of ΔQ in the upper layer is presumably due very largely to direct radiation to outer space. That this outgoing radiation produces no appreciable fall of temperature with increasing elevation, appears to be because the heat of the upper layer is continually replenished by absorption of the radiation from the lower air, but especially because the solar rays are undergoing their initial absorption, and though some of the absorbent material, such as aqueous vapor, is excessively rarefied, there are certain rays which are so powerfully absorbed that they suffer loss in passing through the most tenuous layer.†

The values of R, computed on the above assumption, are considerably greater than those of ΔQ in the lower atmosphere,

* *Op. cit.*, pp. 114-115.

† F. W. Very—Atmospheric Radiation, p. 123.

where we must presume either that atmospheric radiation is itself impeded by vaporous absorption, or that convection plays a larger part in the denser air. The actual mean direct radiation between neighboring air masses, which lies at the foundation of the successive absorption and radiation of the indirect process, must be smaller than that assumed. The extension of an observed air radiation for a layer 1 meter thick, at an excess of 10° , to a layer 1000^m thick with the same excess, or a proportional one, is only justifiable on the supposition that in the passage of heat from molecule to molecule by radiation, the small distances traversed in successive steps compensate for the small differences of temperature and feeble radiations of the separate interchanges whose integral finally reaches a sum total of energy equivalent to that of a direct transmission. Whatever doubt one might have as to the legitimacy of the assumption that the two processes are even moderately equivalent, is now set at rest by the near agreement of the exponent of T for the indirect process with the exponent (4) required by Stefan's law. This seems to prove that, after all, the process is a radiative one, rather than convective.

The potential radiation function which Bigelow derives from the internal energy of the air by the formula

$$K = \frac{U_1 - U_0}{v_1 - v_0},$$

where U_1 and U_0 are the internal energies at the top and bottom of a layer, and $v_1 - v_0$ is the change of volume of unit mass of air in the same interval, at an altitude of 18,000 meters, is about 0.16 of that at the earth's surface, which is 0.4 of that for a black body.* This ratio is not improbable considering the variation of the composition of the air in a vertical column; but a distinction must be preserved between the passage of

* With Kurlbaum's constant of radiation, $R = 5.32 \times (10)^{-4} \times T^4$ joules/sq. m. sec., a black body radiates at 289° and 225° abs. C. (which are temperatures observed in Europe at 0 and 18,000 meters) 3,711,000 and 1,363,000 mechanical K.M.S. units, or 0.532 and 0.196 small calories per sq. cm. per min. (Ratio = 2.71 : 1). Bigelow obtains a ratio of potential air radiation = 6.37 : 1. The sum of the values of the radiant potential (K) between the surface and 18,000 meters altitude is about one-third of the difference for black radiators at the given temperatures, which may mean that the emission bands of the air spectrum cover about one-third of the entire range. On rising in the air some of the vapor bands become narrower and drop out, and thus the potential radiant function diminishes more rapidly than that of the black body for the same fall of temperature. The air radiation from laboratory measurements agrees with the average ΔQ , which therefore represents the actual air radiation to space and increases upwards with the progressive removal of the outer obstructing layers. The surface layers of air have large K and small ΔQ of necessity, for it is only because these layers are not free to radiate to space in accordance with their high potential that the lower air can maintain its relatively high temperature.

energy through the atmosphere by the modified radiant process, outlined here, and a pure radiation. The sudden increase in the constant second differential of Q at the isothermal level, strongly suggests an accession of immediate radiation to space above this point, and a progressive diminution of the indirect radiant process from thence outward, together with a cessation of aqueous condensation which supplies considerable heat to the lower layers, while further loss of temperature is only permitted through the gradual removal of absorbent substances which prevent the passage of radiation of great wavelength, characteristic of still lower temperatures.

The methods employed by Bigelow still retain something of empiricism. Wherever a temperature gradient less than that of the adiabatic rate prevails in the atmosphere, some heat must have been supplied by radiation, or by condensation of aqueous vapor, or in other ways; and this extraneous addition is not taken into account by the formula which connects the density with temperature and pressure. It is known from laboratory experiments that the specific heat of air at constant pressure is very nearly constant between -39°C. and $+200^{\circ}\text{C.}$ Wherever the values of C_p computed by Bigelow's formula depart from the true value given by laboratory experiment, the deviation of the fictitious or apparent C_p denotes that only a part of the thermal variation with the altitude is due to simple mechanical transportation and expansion of masses of air. The deviation becomes progressively greater in the upper air where production of heat by absorption of solar radiation is large. From the intimate relation between C_p and R , the gas factor, a corresponding variation is produced in the fictitious value of R . Similarly, if the computed value of the air radiation is larger than that of ΔQ in the lower layers of air, this must mean that the data employed include other phenomena besides those of radiation. Although the upper air is more transmissive than the lower air for radiations of wave length less than 15μ , the final limit to further decrease of temperature by atmospheric radiation to free space appears to result from the virtual opacity of the air to longer waves than these, coupled with the fact that a temperature has been reached at which these long-waved radiations constitute the greater part of the radiant output. This limit is only extended by the very gradual removal of the last traces of absorbent at still greater altitudes. These remarks are not intended as a criticism of the methods, for it is difficult to see how any others can be used, but are made to point out the limitations of an analysis which is obliged to deal with data covering a variety of simultaneous processes in unknown proportions, and in the endeavor to elucidate the meaning of the results.

Although the radiation function in the lower air, where only indirect radiation exists, can be fairly well represented by a radiation formula with the exponent of T (the absolute temperature) equal to 4, so that indirect radiation is still satisfied by Stefan's law with small changes in the constant,* yet in the upper isothermal layer where free radiation ought, if anywhere, to be in control, the exponent of the radiation formula suddenly becomes negative. This discrepancy, however, is more apparent than real, and appears to be due to the superposition of several effects attributable to the progressive removal of absorbent vapor in the upward direction, combined with a special absorption of solar rays and the limitation of long-waved radiation.

The observed value of air radiation has an immediate application to the phenomena of the nocturnal deposition of dew where the atmospheric cooling concerns an air layer only a few meters thick; but this value may require modification when applied to the conditions of the elevated isothermal region. Here the diminished radiant mass in unit volume has the outflow of its radiation of smaller wave-length than 15μ proportionally less obstructed through absorption by its own substance, which tends to give constant radiation in spite of varying density, and thus there is a new freedom of radiation from the upper surface which was not possessed by the air at lower levels, while at the same time there is a strong accession of thermal energy from absorption of the sun's rays by the first portions of aqueous vapor encountered. This absorbent layer immediately becomes a radiant one and its extra heat is dissipated by radiation to outer space. (The region of the accession of freer atmospheric radiation to outer space is about 3000 meters higher in the torrid zone than in temperate latitudes and all of the data are correspondingly modified.) This seems to be the meaning of the sudden increase in the loss of heat on entering the isothermal layer, which passes, according to Bigelow's computation, from -140 in mechanical K.M.S. units per 1000 meters for the lower layers, to -362 per 1000 meters for the isothermal layer.

Westwood Astrophysical Observatory,
Westwood, Massachusetts,
May, 1912.

* We knew already that, within the very limited range of its selective radiation, the maximum radiant layer of a gas behaves like a black body.

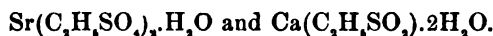
ART. XLVII.—*On the Hydrolysis of Alkyl Metallic Sulphates*; by G. A. LINHART.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxxxvii.]

III. *Ethyl Calcium Sulphate and Ethyl Strontium Sulphate.*

It has already been shown* that for methyl-, ethyl-, and propyl barium sulphates the rate of decomposition in acid solution decreases with increase in the weight of the alkyl group. It was the purpose of this investigation to study the effect, on the rate of hydrolysis, of replacing the barium in ethyl barium sulphate by strontium or calcium.

Preparation and Analysis of the Esters.—The same method was used for the preparation of these esters as that described in the first two papers† of this series. In order, however, to increase the yield the mother liquor from the first crystallization was concentrated on the steam bath and, before filtering through the hot water funnel, was treated with finely divided carbonate of calcium or strontium in slight excess to neutralize the small amount of alkylsulphuric acid formed. In the case of the strontium ester the crystals obtained from the fourth fraction were discarded, as they contained some strontium sulphate, while only the first and second fractions of the calcium ester were free from calcium sulphate. After treating the crystals as described in the second paper‡ of this series, their composition corresponds to the formulæ:



Method of Hydrolysis.—The method of hydrolysis described in previous papers§ was slightly modified. Since these esters gradually lose their water of crystallization, approximately the required amount of the crystallized substance was dissolved in distilled water and the concentration determined in the wet way. Ten cubic centimeters of this solution and 10^{cm³} of hydrochloric acid were introduced into test-tubes of about 40^{cm³} capacity, previously constricted at about 1 1/2 inches from the mouth to a size just large enough to allow the stem of a carefully calibrated pipette to go through and the displaced air to escape. The tubes were then sealed, allowed to cool, shaken and submerged in the thermostat. The hydrochloric acid used contained one gram of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) for every 10^{cm³} to transform the calcium and strontium sulphates, resulting from the hydrolysis of the cal-

* This Journal, xxxiv, 292.

† This Journal, xxxiv, 292.

‡ Ibid., xxxii, 53, and xxxiv, 292.

§ Ibid., xxxii, 53, and xxxiv, 292.

cium and strontium esters, to their chlorides and the equivalent amount of barium chloride to barium sulphate. (The addition of barium chloride slightly retards the rate of hydrolysis of the alkyl barium sulphates, as will be shown in a subsequent paper on the hydrolysis of the alkyl sulphuric acids.)

In the hydrolysis of the alkyl barium sulphates no attempt was made to purify the precipitated barium sulphate beyond washing it with hot water until the wash water was free from chlorine, since on ignition the small amount of included alkyl sulphuric acid was destroyed and the included trace of alkyl barium sulphate was changed to barium sulphate. In the present work, however, the amount of barium chloride included is too great to be neglected, and in order to remove this included barium chloride the precipitated barium sulphate resulting from the hydrolysis was filtered through an ignited and weighed perforated platinum crucible fitted with an asbestos mat, thoroughly washed with hot water, then gently ignited until the mass completely charred. The solid cake thus formed was broken up, care being taken not to disturb the asbestos mat, and again ignited until all the carbon was burned off and the barium sulphide, resulting from the reducing action of the carbon, oxidized to barium sulphate.† The ignited and cooled precipitate was again washed with hot water slightly acidulated with hydrochloric acid to remove any basic chloride which might have been formed during the ignition. The crucible was then gently ignited, cooled and weighed. By this treatment practically all the barium chloride was removed.

Theory.—The calcium or strontium sulphate formed in this reaction, being somewhat soluble in water, is instantaneously and quantitatively removed from the reacting system by combining with the barium chloride present to form barium sulphate. It is the weight of the barium sulphate which is given in grams and gram equivalents in columns two and three in Table I.

The course of the reaction is similar to that of the alkyl barium sulphates described in previous papers,‡ i. e.,



M = Ba, Sr or Ca.

This leads to the mathematical expression

* Some barium sulphide frequently escapes oxidation, but never more than a small fraction of a per cent.

† It is best to prevent caking by piercing the precipitate with a platinum wire just as it begins to char. It then falls to a powder and the carbon and barium sulphide are more easily oxidized. See this Journal, xxxiv, 290.

‡ Loc. cit.

$\frac{dx}{dt} = K(A - 1/2 x)(B + 1/2 x)$, which on integration gives

$$K = \frac{2 \times 2.3}{(A+B)t} \log \frac{(B + 1/2 x)A}{(A - 1/2 x)B}$$

Experimental Results.

TABLE I.

T = 60°

Ethyl Calcium Sulphate in presence of Barium Chloride.

t in hours	BaSO ₄		K
	in grams	in gram equiv.	
	B = 1.0 N HCl		
20.0	0.1000	0.0428	0.00733
42.5	0.2066	0.0885	0.00733
72.3	0.3340	0.1431	0.00726
96.0	0.4288	0.1837	0.00726
120.0	0.5190	0.2224	0.00729
141.0	0.5920	0.2536	0.00729
165.0	0.6656	0.2852	0.00726
α	0.7002	0.3000 = A	

B = 0.5 N HCl			
24.3	0.0570	0.0244	0.00673
42.5	0.0981	0.0420	0.00667
72.0	0.1636	0.0701	0.00667
96.0	0.2117	0.0907	0.00652
140.5	0.3020	0.1294	0.00652
191.0	0.4090	0.1752	0.00661
241.0	0.5050	0.2164	0.00667
286.5	0.5846	0.2505	0.00667
α	0.7002	0.3000 = A	

Ethyl Strontium Sulphate in presence of Barium Chloride.

t in hours	BaSO ₄		K
	in grams	in gram equiv.	
	B = 1.0 N HCl		
22.5	0.1264	0.0541	(0.00828)
48.3	0.2482	0.1063	0.00786
67.3	0.3260	0.1397	0.00761
76.0	0.3700	0.1585	0.00772
96.0	0.4592	0.1967	0.00786
121.0	0.5584	0.2392	0.00789
140.0	0.6248	0.2677	0.00786
α	0.7002	0.3000 = A	

TABLE I (continued).

<i>t</i> in hours	BaSO ₄		K
	in grams	in grain equiv.	
	B = 0.5 N HCl		
22.3	0.0554	0.0237	0.00713
48.0	0.1264	0.0542	(0.00765)
66.7	0.1644	0.0704	0.00719
95.5	0.2378	0.1019	0.00742
139.5	0.3356	0.1438	0.00730
188.5	0.4390	0.1881	0.00725
235.3	0.5280	0.2262	0.00719
286.8	0.6214	0.2662	0.00719
α	0.7002	0.3000 = A	

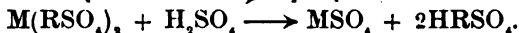
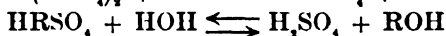
TABLE II.

K for Esters in 1.0 N HCl

Ba(C ₂ H ₅ SO ₄) ₂ *	Sr(C ₂ H ₅ SO ₄) ₂	Ca(C ₂ H ₅ SO ₄) ₂
0.00828	0.00786	0.00733
0.00828	0.00761	0.00733
0.00828	0.00772	0.00726
0.00835	0.00786	0.00729
0.00828	0.00789	0.00729
0.00832	0.00786	0.00726

Summary.—The rate of decomposition of these esters increases with the increase in the atomic weight of the metal, while it decreases in each case with the increase in the weight of the alkyl group, as is shown in the second paper of this series.

2. The hydrolytic decomposition in acid solution of the Ba, Sr and Ca salts of methyl, ethyl and propyl sulphuric acids proceeds very slowly at 60° according to the equations:



3. In order to obtain an integral equation from which to calculate velocity constants the differential equation must take into account the increase in the acidity of the reacting mixture as well as the hydrolysis of alkyl sulphuric acid resulting from the hydrolysis of the metallic alkyl sulphate.

* This Journal, xxxiv, 292.

ART. XLVIII. — *Early Man in America**; by ALEŠ HRDLÍČKA, Curator of the Division of Physical Anthropology, United States National Museum.

AT the request of the Editor of this Journal the writer here presents, in a brief form, the essential data concerning skeletal and to some extent also other remains attributed to geological ancient man on the American continent, more particularly in South America, and the conclusions reached by him and his associates, after prolonged and unprejudiced research into the subject, as to the true age and anthropological significance of these specimens.

Between the years 1899 and 1907 the writer carried out a series of inquiries on the various skeletal remains which suggested or were attributed to ancient man in North America. The studies resulted in a number of publications,† culminating in a memoir comprehending the whole subject, which appeared as Bulletin 33 of the Bureau of American Ethnology. The results of the investigations seemed at first to lend support to the theory of considerable antiquity for some of the remains presented as evidence, as, for example, the two low skulls discovered at Trenton, New Jersey. Subsequent researches, however, cleared up most of the uncertain points, and the entire inquiry seemed to establish the fact that thus far no human bones have come to light in North America representing other than the Indian type of man, which we have many weighty reasons to regard as relatively modern in this part of the world.

The details of the above work are sufficiently well known and easily referred to, and as no further specimens for which geological antiquity is claimed have been brought forth since the publication of the above mentioned report, the territory north of Panama need not be further dealt with in this place.

More interesting and much more complex conditions than those in regard to early man in North America have arisen in

* Published with the permission of the Secretary of the Smithsonian.

† The Crania of Trenton, N. J., and their Bearing upon the Antiquity of Man in that Region. In Bulletin of the American Museum of Natural History, xvi, Art. 3, 23-62, 3 charts, fig. 1-4, pl. i-xxii. New York, Feb. 6, 1902.

The Lansing Skeleton in American Anthropologist, N. S., V, 323-330, 1 fig., Lancaster, Pa., June, 1903.

A report on the Trenton Femur (written in 1902), published with E. Volk's The Archeology of the Delaware Valley, Memoirs of the Peabody Museum, v, Cambridge, Mass., 1911, pp. 244-247.

Skeletal Remains Suggesting or Attributed to Early Man in North America. Bulletin 33 of the Bureau of American Ethnology, 1-113, pl. i-xxi, fig. 1-16, Washington, 1907.

South America. In the latter continent skeletal remains of man, which came to be regarded as of geological antiquity, have been accumulating since the forties of the past century, and by the end of the last decade had multiplied to such an extent and had become so important, as to call for the closest attention on the part of anthropologists. Moreover, frequent reports were made of finds of fossil animal bones charred, striated, perforated or broken by human agency in the far past; of burnt earth and scorix showing human activities deep in the Pampean times; and we were even told of whole cultures, represented by numerous archæological objects, belonging to the Quaternary or even the Tertiary. Finally, the scientific world was startled by an announcement of remains of not merely a number of distinct ancient species of man, but also of several human precursors, supposed to be connected, somewhere in the Eocene, with the little South American primates of that period.

It will be useful to introduce a condensed chronologically arranged account (pp. 546-548) of at least the skeletal material upon which rests the contentions that geologically ancient man existed in South America.

It was principally on the basis of the finds shown in this chart that Professor Florentino Ameghino, the Argentinian paleontologist and author who was in the largest degree responsible for these reports, has formulated a far-reaching theory regarding not only the presence of early man in South America, but also man's descent and his migrations, which, if definitely established, would greatly enlarge and modify our scope of vision.

On close inspection, however, the records of the finds of the supposedly ancient remains, the descriptions of the specimens themselves and the deductions drawn from the material, as a rule were found to be unsatisfactory. They were full of defects and uncertainties which, in view of the importance of the subject, were most perplexing and owing to the remoteness of the field and other difficulties, appeared as insurmountable obstacles to the formation of a definite opinion on the merits of the evidence; indeed the whole subject threatened to become a tangle which might never be unraveled.

It was under these conditions that the Smithsonian Institution in 1910 sent to South America, and particularly Argentina, an expedition consisting of the writer and of Mr. Bailey Willis, a geologist of much experience with formations such as were to be met with in the course of the investigation. The objects of this expedition were to gain as far as possible a clear view of the whole problem of early man in the southern continent; to examine the original specimens relating to the subject; to study at least the principal localities and deposits from

which ancient human remains had been reported and ascertain on the spot, if still feasible, the exact circumstances of the finds; and to discover if possible and collect additional osseous, archeologic, or other specimens bearing on man's antiquity.

After a brief stop in Brazil, Argentina was reached in May, 1910, and the stay of the writer in the country lasted two months, while that of Mr. Willis was somewhat longer. The Argentina men of science received us very cordially and facilitated our work with a great liberality. Florentino Ameghino and his brother Carlos were particularly helpful. The specimens which it was important to examine, even those the descriptions of which had not yet been published, were placed freely at our disposal. Ameghino and his brother accompanied us, notwithstanding the inclement season, for nearly three weeks from point to point along the coast where vestiges of ancient man or his forerunners were believed to have been discovered, and others went with us to more distant parts of the country. We found skeletal remains in the same localities and under the same conditions as some of those previously reported as ancient, and collected others that threw much needed light on some of the important points involved. Several thousands of archeological specimens bearing on the supposedly ancient cultures were discovered in undisturbed positions and collected; and many samples of fossil bones and shells, as well as of loess, various concretionary deposits, burnt earth and scoria, supposed to be of ancient human origin, with other articles, were gathered and brought back with us for further investigation in our laboratories.

After the return of the expedition to Washington the gathered data and specimens were subjected to considerable further studies and comparison, and a large amount of recent human skeletal material from South America was examined by the writer. The archeology was taken up by Professor W. H. Holmes of the U. S. National Museum; the petrology by Messrs. F. E. Wright and C. N. Fenner of the Geophysical Laboratory, Carnegie Institution; the shell material was turned over for identification to Dr. Wm. H. Dall of the U. S. Geological Survey, and chemical examinations of numerous bones were conducted under the direction of F. W. Clarke of the same institution.

The results of the several researches were without exception adverse to the theory of the existence of early man and his precursors on the southern continent. Anthropology, geology, archeology, the study of the burnt earths and scoræ, that of the shells which should have established the great age of some of the strata, and the chemistry of the bones, all speak independently and forcibly against the assumed existence

SKELETAL REMAINS ATTRIBUTED TO EARLY MAN IN SOUTH AMERICA.

DATE	LOCALITY	DISCOVERER	HUMAN REMAINS	DEPTH	DEPOSIT	ASSOCIATION	PRESERVED IN	PERIOD
1835 1844	Caves, Lagoa Santa, Brazil	P. W. Lund (naturalist)	Numerous skulls and bones, with 1 stone utensil	Immaterial	Mixture of cave debris and water deposits	Numerous fossils mammals, also many living forms	Museo Lundi, Copenhagen	Quaternary
1864	Rio Carcarañá, Arg.	F. Seguin (collector of fossils for sale)	Teeth, phalanges fragments of bones, stone implements	Moderate	"Pampean" deposits of the river bank; exact place unknown	Extinct horse and bear	Mus. d'Histoire Natur., Paris	Quaternary
1871	Arroyo de Frias, Arg.	F. Ameghino (i. t. a beginner collecting fossils)	Skeleton	?	"Pampean"	Many bones of extinct animals	Sent to Museo Civico, Milan, lost	Pliocene (A.)* Quaternary (L-N.†)
1872 or 1873	"	F. Ameghino	Skeleton, with a few bones from another; stone implements, etc.	9 feet ?	"Pampean"	Hoplophorus, Eutatus, and others	Museo de La Plata, Arg.	
1874	"	F. Ameghino with G. Ramarino	A vertebra and a scapoid	?	"Pampean"	Carpapace of Glyptodon, etc.	" " ?	
1876	A "saladero" near Pergamino, Arg.	S. Roth (i. t. collector of fossils)	Skeleton	9 feet deep	Loess, wall of a gully	-----	Few remnants in Museo Nacional, Buenos Aires	Quaternary
1879	Rio Negro Valley, near Viedma, Arg.	E. P. Morono (explorer)	Two skulls	a) 12 feet b) 6 feet	Alluvia Sand dune	-----	Museo de La Plata (†)	a) "Glacial" time of Patagonia, b) "Ancient"
1881	Fontezuelas near R. Arceifes, Arg.	S. Roth	Skeleton, an implement from deer horn	Less than 8 feet	"Pampean"	Under upturned carapace of Glyptodon	Museo Lundi, Copenhagen	Pliocene (A.) Quaternary (L-N.)

*Florentino Ameghino.

†Lehmann Nitsche.

1882	Arroyo de Samborombón, Arg.	E. de Carles (traveling naturalist Museo Nac.)	Skeleton	About 4 feet (?)	" Lacustrine Pampean " in bank of the stream	Scelidotherium (?)	Museum at Valencia, Spain	Pliocene (A.) Quaternary (L-N.)
1882	Monte Hermoso, Arg.	Employee of Museo de la Plata	Atlas ("Tetraprothomo," "Homo neo-gaens")	(?)	Loess; nature?	(?)	Museo de la Plata	Miocene (A.) Tertiary (L-N.)
1887	Baradero, Arg.	S. Roth	Skeleton	3 feet (?)	" Intermediary Pampean "	(?)	École Polytechnique, Zürich	Tertiary
1888 (?)	Rio de Arrecifes, Arg.	M. Monguilot (preparator Museo Nac.)	Skull	(?) Moderate	" Pampean "	(?)	Facultad de Filosofía y Letras, Buenos Aires	Quaternary
1888	Miramar, Arg.	A Canessa (employee of Museo de la Plata)	Skull ("H. Pampeus")	(?) Small	" Pampean "	Scelidotherium, etc. (?)	Museo de la Plata	Pliocene (A.) Quaternary (L-N.)
1888 (?)	Arroyo, Chocorí, Agr.	F. Larrumbe (employee of Museo de la Plata)	Skeleton	Surface layer	" Pampean "	(?)	" "	Quaternary
1896	Buenos Aires	Laborers	Skull-cap ("Diprothomo")	About 40 feet (?)	Sand, under "Tosca"	— (Glyptodon slightly higher at distance)	Museo Nacional, B. A.	Pliocene (lowest level)
190-	Monte Hermoso	Carles Ameghino	Femur ("Tetraprothomo")	(?)	Tertiary "Pampean"	Numerous long extinct animals	" "	Miocene
1906 1908 ?	Río Dulce and Río Hondo Ovejero, Arg.	E. de Carles	2 skulls and some bones with potsherds	About 3 feet	" Superior Pampean "	Guanaco ?	" "	Quaternary

SKELETAL REMAINS ATTRIBUTED TO EARLY MAN IN SOUTH AMERICA—Continued.

DATE	LOCALITY	DISCOVERER	HUMAN REMAINS	DEPTH	DEPOSIT	ASSOCIATION	PRESERVED IN	PERIOD
	Above Ovejero	E. de Carles	Skull and parts of bones	(?) Less than 8 feet	"Superior Pampean"	-----	Museo Nacional, B. A.	Quaternary
	Sotellillo	"	Skull and a part of another, fragments of bones	Over 20 feet (?)	"	-----	"	"
	La Cañada	"	Portion of skull and bones	About 6 feet	Alluvium	Femur of Megatherium, nearby -----	"	"
	Sotelo	"	Skull of infant, parts of bones	Near surface	"Superior Pampean"	-----	"	"
1907	Necochea, Arg.	L. Parodi (gardener)	Skull and fragments of bones	Surface layer	Denuded "Pampean"	-----	"	Pliocene (A.)
1910	"	"	Skull, with fragments of another	Surface layer	"	-----	"	Quaternary (L-N.)
1910	Leguna Malacara	A sailor	2 skeletons ("Homo sinemonto")	Fossa in surface layer	"	Glyptodon, Scelidotherium, etc., at some distance -----	"	"
1910	Necochea	L. Parodia (gardener)	Parts of a skeleton	Surface layer	"	-----	U. S. Nat. Mus.	"
1910	Arroyo Siago, Arg.	Carlos Ameghino	Skeleton ("Homo caputclintus")	5½ feet (?)	"Pampean" loess	(Glyptodon once found in same deposit in the neighborhood)	Museo Nacional, B. A.	Pliocene

of ancient human or of any prehuman forms in South America. The evidence obtained attests nothing more than the presence in the south, as similar evidence has formerly shown in the north, of the already differentiated and relatively modern American Indian.

The bibliography of the subject, the historic data, the details which led to the above conclusions, will be found in a volume recently published by the Bureau of American Ethnology* and need not be here repeated. The only question which requires to be dealt with in this place is that of the causes which have led to the remarkable conclusions concerning the antiquity of man in South America reached by Ameghino and other South American men of science who have occupied themselves with the problem. How has it come about that a number of investigators, including Ameghino, the foremost exponent of South American paleontology, have arrived at, maintained and even strenuously defended conclusions, which after a serious and allsided research into the subject, cannot be accepted and must in fact be entirely subverted by other students.

The causes may never be fully analyzed but comprise, in the main, defective collection, imperfect criteria of comparison, a lack of experience in anthropology, and finally, in at least some cases, the allure of the new and wonderful.

As to defective collection, it may be said that with the sole exception of the Lagoa Santa material, not one of the specimens advanced as representing early man in South America was gathered in a way to satisfy the requirements of science. Let us turn to the records:

The "Rio Carcarañá" bones were brought to Buenos Aires by F. Seguin, a collector and dealer in fossils. No written report was ever made regarding the circumstances of the find by Seguin, his oral information was very deficient in details, and the stratum from which the bones came, their association, and even the place where the discovery was made are uncertain. The first "Arroyo de Frias" find was made about 1871 by F. Ameghino, at that time less than 18 years old, acting as a "subpreceptor" at a nearby school and beginning to interest himself, while searching to regain lost health, in fossil bones.† The "Saladero" skeleton was found in 1876 by Santiago Roth, at that time a young collector of fossils, and was not even mentioned in literature until twelve years later. At the time of its discovery the bones were thought nothing of and were given to

* *Early man in South America*, by Aleš Hrdlička, with the collaboration of W. H. Holmes, Bailey Willis, Fred. Eugene Wright and Clarence N. Fenner. Bull. 52, Bureau American Ethnology, Smithsonian Institution, Washington, D. C., 1912, 8vo, pp. i-xv, 1-405, with 68 plates and 51 figures.

† See "Dr. Florentino Ameghino," por Juan B. Ambrosetti, *Anales de Museo Nacional*, etc., Buenos Aires, xxii, page xii.

a companion. About one year later Roth happened to see in the garden of his companion some fragments of "fossil" bones and on asking where they came from he was informed that they were the remnants of the skeleton dug out near Saladero. And these fragments constitute the sole evidence of the Saladero representative of the ancient man of Argentina.

The "*Arrecifes*" skull was found by a preparator attached to the Museo Nacional of Buenos Aires "in terrane belonging to the Pampean formation which was left exposed by water." This is absolutely all that has ever been recorded in regard to the circumstances of this discovery. The "*Samborombón*" skeleton was found in 1882 by a traveling naturalist of the Museum at Buenos Aires, and the first meager details regarding the specimen were not given until 1889. The skeleton itself is lost without ever having been studied, but nevertheless poses as a representative of "fossil" man in Argentina, and has even given rise to the coining, by Kobelt in Germany, of a new human species, the "*Homo pliocenicus*." The "*Chocorí*" skeleton was found about the year 1888 by an employee of the La Plata Museum. The first notice of it was not published until nineteen years later. The remains lay "abandoned on the surface of the ground, partly covered by indurated sand." The "*Ovejero*" bones were collected at different times by one of the traveling naturalists of the Museum at Buenos Aires. They were found at different levels in wind-blown loess in the proximity of a fair-sized river, and in association with the bones of several recent forms of animals.

The "*Baradero*" skeleton lay with most of the bones in their natural relations in eolian loess, about 3 feet deep below the surface. The "*Arroyo del Moro*" skeleton, which gave rise to the new species of *Homo sinemento*, was discovered by a sailor and his wife, and later excavated at the initiative of a local physician by the sailor, his boy, and a gardener. The "*La Tigra*" skull, which resulted in the establishment of *Homo pampaeus*, attributed to the Tertiary, was found in 1888 by an unscientific employee of the Museo La Plata near the Arroyo La Tigra. The employee was charged with collecting fossils for the Museum. He went to a point at which fossil animal bones were previously discovered, excavated in the neighborhood, and among other things discovered a human skull. This is all we know of the circumstances of the discovery of this specimen, which has been given such importance. Another small lot of bones relating to the *Homo pampaeus* were discovered on and near the surface of some partly denuded ground near Necochea by the above mentioned gardener. The "*Dipprothomo*" (or nearest but one precursor of man) fragment was found by common laborers and for thirteen years lay unnoticed in the

Buenos Aires collections. As to the "*Tetraprothomo*" (the fourth precursor of man, counting backward from the latter), finally, the atlas was brought by an employee of the Museo de la Plata from a fossil collecting trip to Monte Hermoso, and no details are known of this discovery, even the year of the find being uncertain; while the femur was found, with other fossil bones, some time during the early years of the present century, the exact year being also uncertain, by Carlos Ameghino. The atlas, which is human, after being brought to the Museum was forgotten and lay for many years unnoticed. The first published notice of it appeared about twenty years after its discovery. The femur belongs to an ancient small-sized carnivore.

The above notes could be extended; however, the subject may be briefly summarized by the statement that not one of the osseous specimens which represented the "ancient" man in South America and particularly in Argentina has been discovered or exhumed by an experienced anthropologist or archeologist, or by a person well trained in or employing the methods recognized to-day as requisite in dealing with objects of such importance. And this applies equally to the other objects than human bones which represent the "early" man in Argentina. A more meager and defective record could scarcely be imagined.

Following unscientific collection of the specimens came defective judgment in adjusting their age and, in the case of numerous specimens other than human bones, of recognition of their true character. Such defects of judgment were, as has appeared from the observation of Mr. Willis, an imperfect and in some instances decidedly faulty identification of the deposits in which the human remains were discovered; a general but wholly unwarranted conclusion that the human bones were contemporaneous with the deposit in which they lay and with the bones of various animals found at the same levels; the noxious opinion that the mineralization of a human bone meant generally and of necessity a great antiquity of the specimen; the assumption that certain refuse and by-products of the manufacture of stone implements were sufficient to establish ancient and otherwise unknown primitive cultures; the failure to recognize or admit the accidental nature of numerous markings on the bones of ancient animals; and the attributing of anthropic significance to baked earth and scoriae which are in all probability secondary volcanic products having nothing to do with man's existence.

A lack of experience in anthropology, with a dearth of material for comparison, resulted in such sad occurrences as the giving of wholly faulty positions to more or less incomplete human crania and ascribing the apparent differences

which they presented in consequence, to morphological inferiority ; in giving undue weight to various actual features which, with a more extensive view, would have been seen to be well within the limits of variation of the same parts in man and particularly in the Indian of the present day ; and above all, in the failure in numerous cases to recognize an artificial deformation of the skull, with the mistake of taking the results of such deformation, particularly the lowered forehead, for marks of anthropological inferiority of the specimen, and even regarding them as species characters.

In conclusion it cannot be denied that in at least some cases the part of a proper critical analysis has been taken by the more enticing and less difficult task of enthusiastic theorization, one of the most striking examples of this being Ameghino's hypotheses about the various "Precursors."

All the above points are dealt with in detail in the main report of the writer and his collaborators on this subject and therefore a further discussion of them in this place would be quite superfluous ; but it may not be amiss to give here just a few concrete instances illustrating the conditions.

The Argentinian writers did not hitherto clearly distinguish the holocene and the Quaternary in the pampas deposits ; most often everything beneath the vegetal layer was regarded as a part of the Pampean formation and as of definite geological age ; yet the upper and sometimes large portions of the deposit are evidently of a very recent origin, the paleontological remains which they hold being of secondary inclusion. Many uncertainties exist also in the recognition of the Tertiary as distinguished from the Quaternary Pampean deposits.

One of the most important strata in relation to ancient man, the so-called "Interensendeian" of Ameghino, could not be traced at all by the geologist of the Smithsonian Expedition, and what was pointed to by Ameghino himself as representing this layer, proved to be a modern sea shore agglomerate of shell detritus and sand, containing remnants of molluscs of living species only. And at Ovejero, what was represented as a Quaternary Superior Pampean bed was found to be nothing but a wind-blown deposit of no great age.

In a number of instances, particularly at "Necochea" and Arroyo del Moro, the human remains recovered represented clearly burials and, hence, introductions into the earth ; yet they were described as contemporaneous with the deposits which they barely penetrated.

Mineralization of the human bones was taken invariably as proof of the great age of the specimen, notwithstanding the well-established fact that it depends far more upon the environment than upon time. Actually not a single perceptibly mineralized human bone was seen by the Expedition in Argentina

which was not regarded by one or more of the local scientists as geologically ancient. Yet along the coast and in other places, on or near the surface of the ground, lay many bones of domestic and other animals of living species showing plainly various phases of "fossilization." Really no bones from burials or inclusions in the Pampean deposits were met with that were not more or less mineralized, which is easily explainable by the high percentage of calcareous and other mineral contents favoring "fossilization" that are held by the formation.

The results of lack of experience in anthropological matters manifested itself especially and painfully in the case of the "Diprothomo." This form is represented by a frontal bone with a portion of the parietals. The fragment was described, not in the position which it would occupy in a normally poised skull, but in that which it assumed when laid on the table. This error was responsible for the creation of a genus of human ancestors.

The descriptions of various specimens extended to and made much use of minute details, which are known to be of little or no biological significance. In the cases of the *Diprothomo* and *Tetraprothomo*, as published by Ameghino, there are page upon page of minutiae through which even a trained anatomist wades with difficulty and which only obscure the true character of the specimens. The Monte Hermoso atlas, which in every respect is well within the range of variation of the same bone in the prehistoric and probably even in the historic American Indian, was at the same time and largely by such minutiae being made a part of the *Tetraprothomo* by Ameghino, and given as a representative of a Tertiary species of American man by Lehmann-Nitsche.

As to the part that theory played in this connection, it is sufficient to point to the system of human descent and migration constructed on the basis of the various reports assumed to indicate the presence of human man in South America by Ameghino. He not only derived the whole human family from certain little primitive forms in South America and peopled that continent with hitherto unsuspected species of man and genera of precursors, but he also considered that all these species and genera became extinct before South America was peopled by the Indians. The latter, he assumed, came from the emigrants who originally left the southern continent and spread over Africa, Asia, and North America, finally reaching again the southern part of the continent.

The above examples could be much enlarged upon, but this is hardly necessary in view of the facility with which the detailed report on "Early Man in South America" can be consulted. Here it is only just to the other South American

authors who are involved in this subject to say, that the majority of the failures referred to were those of the principal exponent of ancient man in Argentina, Florentino Ameghino. And lest the above examples may seem partial and unjust the interested reader is strongly urged to peruse the detailed accounts of these matters.

The conclusions which the members of the Smithsonian Expedition inevitably reached and hold in regard to early man in South America were as follows:

An unbiased study of all the available facts has shown that the whole structure erected in support of the theory of geologically ancient man on that continent rests on very imperfect and incorrectly interpreted data and in many instances on false premises, and as a consequence of these weaknesses must completely collapse when subjected to searching criticism. It fails to establish the claim that in South America there have been brought forth thus far tangible traces of either geologically ancient man himself or of any precursors of the human race.* The position is maintained, and should be maintained, it seems, by all students, that the final acceptance of the evidence on this subject cannot be justified until there shall have accumulated a mass of strictly scientific observations adequate in kind and volume to establish a proposition of so great importance.

* In the opinion of the writer, based on the published data as well as a personal examination of the specimens, the recent "ancient" or "prehistoric" man found in Peru and reported on by Professor Bingham, offers nothing which would necessitate a recasting of these conclusions.

ART. XLIX.—*The Constitution of Some Salic Silicates*; by
HENRY S. WASHINGTON.

Introduction.—In this paper is suggested an explanation of the chemical constitution of the feldspars, lenads, scapolites, and zeolites, which accounts for the intimate relationships that they show. In brief, the hypothesis is that they are aluminosilicates, possess a chemical feature in common, the presence of certain atomic groups, and that the formulas of the feldspars, lenads,* and zeolites, are of identical type, while that of the scapolites is different but closely analogous.

The difficulties presented by the silicate minerals in the study of their molecular constitution are so great, especially as compared with organic compounds, that we are still only on the threshold of knowledge adequate for discussion, and any suggestions put forth at the present time must be regarded as tentative and speculative. Still, certain facts are known, and these, with recent applications of physical chemistry to mineralogy, give justification for dealing with the subject.

The literature of the mineral groups mentioned is so extensive that it cannot be gone into exhaustively here, and only a few of the more recent papers will be mentioned.

Relationships.—The minerals of the four groups under consideration are alike chemically in being silicates of aluminum and of potassium, sodium, or calcium, any two or all three of the last being often present together. Some feldspars contain barium in place of calcium, and this element and strontium are present in a few zeolites, while lithium is essential in encryptite. All the minerals containing these elements, however, are of very rare occurrence. The function of the invariably present aluminum is unknown, though it is generally assumed to be present as a base. The zeolites and analcite are hydrated, containing either water of crystallization, acid hydrogen, or constitutional hydroxyl, in either case very loosely combined. None of these minerals ever contains magnesium, ferrous or ferric iron, manganese, titanium, boron, or fluorine, as essential constituents, in this differing radically from the large and important groups of the pyroxenes, amphiboles, micas, garnets, vesuvianites, epidotes, tourmalines, and olivines. The scapolites alone may contain small amounts of Cl and SO₂. These are also present in the minerals of the sodalite group, which show some affinities with the lenads, but which are now usually

* The name lenad has recently (C. I. P. W., Quant. Class. Ign. Rocks, Chicago, 1908, p. 132) been proposed to replace the term feldspathoid, including leucite, nephelite and their congeners, and this will be used throughout this paper.

regarded as allied constitutionally to the garnets. The heavy metals are never present in nature, though artificial feldspars and lenads have been prepared which contain lead, zinc, silver, or thallium replacing calcium and the alkali metals, and ferric iron replacing aluminum.

In the feldspars, lenads, and zeolites the ratio of $K_2O + Na_2O + CaO$ to Al_2O_3 is constant, 1:1, while in the scapolites the ratio does not differ much from this. The relation of silica to these constituents varies from orthosilicate to trisilicate ratios, and the various minerals are commonly regarded as either orthosilicates, metasilicates, trisilicates, or mixed intermediate compounds. That is, in spite of their chemical resemblances and other evidences of close relationship, presently to be noted, they are usually regarded as salts of at least three distinct silicic acids.

The intimate chemical relations between these minerals and mineral groups are also evident from their alterations in nature and from experiments which have been made in their artificial reproduction. The feldspars are quite readily alterable, changing into scapolites and zeolites, as well as to muscovite, zoisite, and so forth. Feldspars, nephelite, analcite, and other zeolites are common natural alteration products of leucite, and leucite and analcite are readily transformable artificially, the reaction being reversible. Pseudo-leucite will be mentioned later. Nephelite readily alters, especially to analcite and zeolites, and analcite has been formed artificially from some feldspars, as andesine. The scapolites are often derived from the sodicalcic feldspars and are easily alterable themselves, forming a varied number of products, among which the zeolites do not often occur. The zeolites are always secondary, with the exception of analcite in some igneous rocks, and are generally derived from feldspars and lenads, of which most of them are commonly regarded as hydrated forms. Many of them yield feldspars on fusion. Kaolin is the most usual end product of the alteration of the feldspars, lenads, scapolites, and also the zeolites.

The crystallographic similarities and relations between the minerals of these groups, as the feldspars and leucite, and the feldspars, lenads, and zeolites, are commented on by several authorities, as Dana and Hintze, and only need mention here. It also seems scarcely necessary to dwell on the intimate relationship shown by the feldspars and lenads in igneous rocks, as their petrological importance and mutual relations are too well known to need more than mention.

Behavior with Acids.—Of apparently minor importance, but with bearing on their constitution, as will be seen later, is the action of hydrochloric and other acids on the various

minerals under discussion. A brief recapitulation will suffice here. Some of the feldspars and scapolites, as orthoclase, albite, microcline, and marialite, are entirely unattacked. Leucite is soluble, with production of pulverulent silica, while nephelite, anorthite, and many zeolites are easily soluble, giving gelatinous silica. In general, resistance to the attack of acid increases with the silica content, but the bases seem to have little influence, leucite, nephelite, and anorthite being about equally soluble.

Polymorphism.—A very marked characteristic common to the feldspars, lenads, and zeolites is the frequent dimorphism or polymorphism of their molecules, though certain cases (the monoclinic feldspars) may rather be attributed to polysymmetry. Examples are: orthoclase and microcline; albite and barbierite,* the recently discovered monoclinic soda-orthoclase; nephelite and the triclinic carnegieite; anorthite, celsian (the monoclinic barium salt), and the presumably hexagonal form present in calcic nephelite; kaliophilite (phacolite) and the artificial triclinic, isometric and tetragonal (?) forms of the same molecule;† dimorphous leucite, which is enantiomorphously transformable at about 500°; heulandite and epistilbite, and possibly laumontite and levynite; and dimorphous analcite.

The existence of pseudo-leucite, an intimate mixture of orthoclase and nephelite with the crystal form of leucite, is of interest and importance in this connection. There are good grounds for rejecting the usual view that it is a pseudomorph in the ordinary sense, by which soda has partially replaced the potash of an original leucite, and for considering it as representing an original definite and distinct, sodi-potassic, leucite-like mineral, which is only stable at high temperatures and which breaks down on cooling into a microscopic mixture of $(K,Na)AlSi_3O_8$ and $NaAlSi_3O_8$, crystallizing as a sodic orthoclase and nephelite. This view has been previously suggested.‡ The composition of pseudo-leucite from various localities varies somewhat, but the amount of nephelite is always subordinate to that of sodic orthoclase. The most recently described§ calculates out about 52.9 orthoclase, 27.8 albite, and 19.3 nephelite, neglecting the small amounts of biotite and scapolite which are present. This is approximately ($\frac{2}{3}$ or $\frac{1}{3}$ ab).ne., which corresponds to the formula $KNaAlSi_3O_8$, or a molecule each of potassium and sodium leucite with one extra of silica.

* Barbier and Prost, *Bull. Soc. Chim.*, vol. iii, 1908, p. 894. Gonnard, *Bull. Soc. Geol. Fr.*, vol. xxxi, 1908, p. 303. W. T. Schaller, *this Journal*, vol. xxx, 1910, p. 358.

† Z. Weyberg, *Centralblatt Min.*, 1908, p. 395.

‡ C. W. Knight, *this Journal*, vol. xxi, 1908, p. 71. H. S. Washington, *Jour. Geol.*, vol. xv, 1907, p. 387.

§ C. W. Knight, *op. cit.*, p. 292.

A closely analogous substance is "sigterite," originally described by Rammelsberg* as a new plagioclase, but which was later shown by Tenne† to be an intimate mixture of albite and nephelite, though with well-defined cleavage and polysynthetic twinning lamellae. Rammelsberg's analysis yields the composition 26 orthoclase, 13 albite, 60 nephelite, or ($\frac{2}{3}$ or $\frac{1}{3}$ ab), ne. He assigns to the supposed feldspar the formula $(\text{Na}, \text{K})\text{Al}_2\text{Si}_2\text{O}_6$, and it is noteworthy that this is closely like the formula which represents the composition of the Linosa anemousite,‡ $(\text{Na}, \text{Ca})\text{Al}_2\text{Si}_2\text{O}_6$, which has been shown to be a solid solution or mixed crystal of labradorite (Ab, An) and carnegieite, the triclinic form of $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_6$.

The fact that the stable mixed crystals of anemousite contain only 5.6 per cent of the carnegieite molecule, while sigterite, with about 60 per cent of the hexagonal form of the same molecule, evidently represents a mixed crystal which is unstable at ordinary temperatures, is in harmony with the suggestion made in the paper cited as to the limited miscibility of the isodimorphous $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_6$ and $\text{CaAl}_2\text{Si}_2\text{O}_6$; and serves to confirm our views as to the comparative instability of the triclinic form of the former. Taking these facts and the observed cleavage and twinning into consideration, there is little doubt that sigterite represents an original mineral, with triclinic plagioclase-like form, to which the name sigterite would be applicable, but which is unstable at ordinary temperatures.

A somewhat similar case is the alteration product of spodumene, the so-called β -spodumene, described by Brush and Dana.§ This is an intimate mixture of 67.6 albite and 32.1 eucryptite, and may be expressed by the formula $\text{NaLiAl}_2\text{Si}_2\text{O}_6$. This does not seem to be a case of metastability, as with the preceding, but rather due to replacement through weathering. It will be discussed in a later paper on the constitution of the pyroxenes.

Isomorphism.—Isomorphism is the relation between two or more crystalline compounds of identical type of chemical formula and essential agreement in crystal form; the constituent atoms being replaceable by elements or atomic groups of the same valency and similar chemical character and func-

* Rammelsberg, Neues Jahrb., vol. i, 1890, p. 71.

† Tenne, Neues Jahrb., vol. ii, 1897, p. 206.

‡ This Journal, vol. xxiv, 1910, p. 57. Professor F. Zirkel (letter dated 10, III, 1910) kindly called my attention to the fact that the composition of some of the feldspars of the Monte Amiata toscanites, described and analyzed by J. F. Williams (Neues Jahrb. Beil. Bd., vol. v, 1887, p. 419-421), is closely like that of the Linosa feldspar. The analyses are not satisfactory, having been made on small amounts of material and the silica determined by difference, but the general resemblance is striking, and they all calculate out with notable amounts, up to 13 per cent, of the $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_6$ molecule, presumably present as carnegieite.

§ Cf. Dana, Syst. Min., pp. 368 and 426, 1892.

tion; this functional substitution (isomorphous replacement) involving only slight (morphotropic) change in the crystal form, and the isomorphous compounds (mutually either wholly or partially miscible) forming homogeneous mixtures whose properties (chemical and physical) are continuous functions of their composition.

The replacement* may be complete, as is illustrated by barite and celestite, or apatite and mimetite, and an element can be replaced by an atomic group (radical) of like valency, as K or Na is replaced by NH_4 , or F by OH. Isomorphously replaceable elements or radicals may partially replace each other, their total molecular amounts being equal to that needed to satisfy the formula. This is of very rare occurrence or quite unknown among organic compounds, but is so frequent among minerals that examples need not be given. Finally there is a third type of isomorphous replacement, namely, that between atomic groups of the same *total* valency. Thus a bivalent atom or radical replaces or is replaced by two univalent ones, two bivalent atoms by a univalent and a trivalent one, or two trivalent atoms by three bivalent ones, and vice versa. This is illustrated by the mutual isomorphous replacement of Ca and Na, in many silicates, of Pb and Cu, in sulpho-salts, of CaMg and NaFe''' in the pyroxenes, and so on.

These last mentioned atomic groups differ from radicals in the ordinary sense. In radicals the atoms are linked together, and the valency of the group is that of the free bond or bonds, and may therefore be spoken of as *residual*. In the last case the atoms are not linked together between themselves, but are in stoichiometric ratios and together replace a number of other atoms the sum of whose valencies is equal to theirs. While apparently not joined together *inter se*, they act together, and the valency of such a group may be spoken of as *total*. Our knowledge of this sort of replacement is comparatively recent and is still not well understood, but so many examples are known that it is now generally accepted.† As this type of atomic group is of importance in mineralogy and the study of isomorphism, it will be well to distinguish it from the ordinary radical by a special name. For this the word "*integral*" seems to be appropriate,‡ and by this term such atomic groups will be known in this paper.

To sum up, the fundamental characters of isomorphism or isomorphous replacement are *adherence to the same type of chemical formula and agreement in crystal form and structure*, subject to only very slight morphotropic changes,

* Of course actual replacement of a previously present element is not meant.

† Cf. Groth, *Introd. Chem. Cryst.*, New York, 1909, p. 85.

‡ Cent. Dict., "A whole formed of parts spatially distinct or of numerical parts." Standard Dict., adj. "constituting a completed whole"; noun, "a function of variables that remains constant."

the replacement being between elements or atomic groups of like valency, either residual or total, and the physical properties being continuous functions of the composition.

Based on these criteria the sodi-calcic feldspars form a perfectly isomorphous series so far as their crystallographic and physical properties, both scalar and vectorial, are concerned. This is abundantly shown by many researches, especially those of Day and his colleagues,* and Groth† also points out that they possess almost identical equivalent volumes. Similarly the orthoclase-celsian series and the scapolites, chabazites, and other zeolite groups, form crystallographically and physically typical isomorphous series of mineral salts.

But from the chemical point of view the usually accepted formulas of the end members, of which we have every reason to believe that these several series are composed, are not identical in type and therefore do not conform with the definitions and fundamental conceptions of isomorphism as generally understood. Thus the formulas of albite, $\text{NaAl}_2\text{Si}_2\text{O}_8$, and anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, are not of the same type, one being that of a trisilicate and the other of an orthosilicate. The same is true of orthoclase and celsian. In the scapolites the formulas of the end members as interpreted by Tschermak are open to the same objection. Marialite, $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8\text{Cl}$, and meionite, $\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8$, are not identical in chemical type and are therefore not in accord with the accepted criteria of isomorphous substances.‡ The same objection may be brought against the formulas suggested by Groth, $\text{Na}_2(\text{AlCl})\text{Al}_2(\text{Si}_2\text{O}_8)$, and $\text{Ca}_2(\text{AlO})\text{Al}_2(\text{Si}_2\text{AlO}_8)$. Similar non-conformity with the theory of isomorphism is found in the accepted formulas of the end members of the phillipsite and chabazite groups among the zeolites.

The complex and somewhat variable composition of nephelinite, with its content of potash and excess of silica, is apparently inconsistent with its evident crystallographic isomorphism with kaliophilite, eucryptite, and artificial, purely sodic nephelinite. The composition of nephelinite has been variously explained. Following the suggestions of Rammelsberg and Doelter it is usually assumed that a leucitic molecule is present. More recently Morozewicz§ suggests that the nephelites are a series of compounds of the general type $\text{K}_n\text{Na}_n\text{Al}_{n+1}\text{Si}_{n+1}\text{O}_{4n+10}$, with a less common basic series. The best analyses of nephelinite can be interpreted in terms of these molecules, but Foote

* Day, Allen, etc., Carnegie Publication, No. 31, 1905.

† Groth, *Introd. Chem. Cryst.*, New York, 1906, p. 86.

‡ It is noteworthy that the same criticism applies to the formulas suggested by Tschermak for the end members of the pyroxenes, amphiboles, micas, and chlorites.

§ Morozewicz, *Bull. Acad. Sci. Cracovie*, 1907, p. 958.

and Bradley* justly criticise this interpretation as being "open to the serious objection that a chemical compound, so far as we know, does not vary in type. Isomorphous replacement, for instance, varies the composition, but the type of compound remains the same." This remark applies equally well to the usually accepted formulas for the end members of the feldspars and scapolites, discussed above. Foote and Bradley consider that the high silica of nephelite is due to the presence of silica in solid solution in $\text{NaAlSi}_3\text{O}_8$. Later Schaller† suggests that the composition is to be explained as an isomorphous mixture of the crystallographically hexagonal forms of the compounds $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , and a hypothetical hexagonal and isomorphous $\text{NaAlSi}_2\text{O}_7$. This explanation rests primarily on the assumption that (SiO_4) and (Si_2O_7) are isomorphously replaceable. This view and the practical equivalence in function of these two acid radicals has been especially insisted on by F. W. Clarke, but is open to the general objection noted above of non-conformity with the modern theory of isomorphism. It is, indeed, difficult to conceive of the mutual isomorphous replaceability of a trisilicic and an orthosilicic acid radical, and, as will be seen, such a conception is not necessary in the case of the mineral groups under discussion. In a paper just published Bowen‡ comes to the conclusion, based largely on the preparation of an artificial nephelite, that the explanation suggested by Schaller is correct.

The suggested hypothesis.—Streng§ seems to have been the first to appreciate the non-conformity of the then accepted formulas of the end members of the feldspars with the theory of isomorphism as enunciated by Mitscherlich, and in order to render them of the same type suggested the doubled formulas $\text{Na}_2\text{Si}_2\text{Al}_2\text{Si}_2\text{O}_{10}$ for albite and $\text{Ca}_2\text{Al}_2\text{Al}_2\text{Si}_2\text{O}_{10}$ for anorthite. These were adopted and later abandoned by Tschermak. In the different editions of his *Tabellarische Uebersicht*, Groth suggests various structural formulas for the feldspars, and wavers between two types of constitutional formula, namely: $\text{NaAlSi}_2\text{Si}_2\text{O}_8$ and $\text{CaAlAlSi}_2\text{O}_8$ (1882, p. 110), and $\text{Si}_2\text{Si}_2\text{O}_8\text{AlNa}$ and $\text{Si}_2\text{Al}_2\text{O}_8\text{AlCa}$ (1889, p. 137, 1893, p. 156). These, especially the first pair, but somewhat differently written, are essentially those upon which he finally settles, namely, $(\text{NaSi})\text{AlSi}_2\text{O}_8$ for albite (and a corresponding one for orthoclase), and $(\text{CaAl})\text{AlSi}_2\text{O}_8$ for anorthite. These formulas are of identical chemical type, the quinquivalent integrals (NaSi)

* Foote and Bradley, this Journal, vol. *xxi*, p. 30, 1911.

† W. T. Schaller, Jour. Wash. Acad. Sci., vol. *i*, p. 109, 1911.

‡ N. L. Bowen, this Journal, vol. *xxxiii*, p. 49, 1912.

§ Streng, Neues Jahrb., 1865, pp. 411, 513. Cited by Hintze, Mineralogie, vol. *ii*, p. 1431, where a résumé of the early discussion will be found.

| P. Groth, Introd. Chem. Cryst., 1906, p. 86.

and (CaAl) respectively replacing isomorphously the five basic hydrogen atoms of the aluminosilicic acid $H_5AlSi_3O_8$, in accordance with the third method mentioned above. They are, therefore, in conformity with the doctrine of isomorphism and in harmony with the physical isomorphism of the feldspars. These formulas do not seem to have been generally adopted or even much mentioned, though Miers,* speaking of albite and anorthite being respectively salts of polysilicic and orthosilicic acids, says: "But here again the close relationship which undoubtedly exists between albite and anorthite finds no expression. If one is to regard them as similar salts, the radicle $SiNa$ of albite must be replaced by the radicle $AlCa$ of anorthite, so that Al plays the part of an acid." It will be observed that these formulas are essentially those of Streng.

Nothing in theoretical mineralogy is more certain than that the sodi-calcic feldspars form a typically isomorphous series and that the *empirical* compositions of the end members, albite and anorthite, are well ascertained and are represented by $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. What is uncertain is the arrangement and number of atoms in the molecule, that is the constitutional formula, and of what acid or acids they are salts; though their physically perfect isomorphous relations should leave no room for doubt that their formulas must be of identical type and that they are salts of the same mineral acid.

Apart from the fact that minerals are known which are, or can be interpreted to be, salts of trisilicic and orthosilicic acids, $H_3Si_3O_8$ and $H_2Si_2O_8$, we seem to have no real ground for thinking that albite and anorthite must be interpreted respectively as such salts, in accordance with the usually accepted Tschermak's formulas. On the contrary, the now well-established general facts and laws of isomorphism are decidedly against this interpretation, as they are against others of the same mineralogist's end member formulas which are almost universally accepted. Without wishing to detract from, and with full recognition of, the brilliant and invaluable contributions of Tschermak to the science of mineralogy, it may be said that mineralogists have been brought up to accept this view of the feldspar molecules, partly because of the great authority of its originator, partly because it is simple and certainly can express the composition of nearly all feldspars, partly because there is as yet no experimental verification or disproof, and largely because the seriousness of the deviation from the principles of isomorphism is not duly appreciated.

If we accept Streng's and Groth's suggestion of the presence of the totally quinquivalent integrals $(R'Si)^v$ and $(R'Al)^v$, with the decivalent integral $(CaSi_2)^x$ in some cases, it will be

* H. Miers, *Mineralogy*, 1902, p. 209.

found, as is here shown, that the constitution of all the members of the feldspar, leucite, nephelite, and scapolite groups, and nearly all the zeolites, can be interpreted in such a way as readily to explain their composition, mutual relations, polymorphism, isomorphism, resistance to acids, and the relation to the mutually common end alteration product kaolinite.

On this interpretation the feldspars, lenads, and most zeolites are regarded as salts, or isomorphous mixtures of salts, of an alumino-silicic acid, $H_2AlSi_2O_6$, or most probably a polymer of this, the five hydrogen atoms being isomorphously replaced by the integrals $(R'Si)^x$, $(R''Al)^y$, and $(R'Si_2)^z$, R' being K, Na, and Li, and R'' being Na, K, Ca, and rarely Ba and Sr. If one regards all the aluminum as basal this reduces to the general formula of an orthosilicic acid, $(H_2SiO_4)_n$, but it must be noted that it is now becoming generally recognized, in accordance with the effects of mass action of complex acid radicals, as shown by Penfield and by Groth, that aluminum and often ferric iron function, at least in part, in the acid portion of the mineral salt.

The scapolites, on the other hand, while containing the same integrals, which explains their relations to the feldspars, etc., are interpreted as salts of a different alumino-silicic acid, $H_{10}AlSi_4O_{22}$, the hydrogens being entirely replaced by the radicals $(NaSi)_2$ and $(CaAl)_2$. Some modification of this most simple statement may be necessary to explain the presence of Cl and SO_4 , as will be shown later.

It must be supposed that the salts of the fellenadic acid $(H_2AlSi_2O_6)_n$ are polymorphous, in general trimorphous, and this acid may be called for convenience fellenadic acid. The salts of the scapolitic acid seem, on the other hand, to belong only to the tetragonal system, though dimorphism may possibly be discovered in the future. It is noteworthy that, corresponding to the difference in acidic type, tetragonal symmetry does not seem to be represented among the feldspars or lenads, and only rarely among the zeolites.

This interpretation of the feldspars, lenads, etc., somewhat resembles that of F. W. Clarke,* who considers Si_2O_6 and SiO_4 to be "mutually equivalent" and that many minerals which are apparently orthosilicates or metasilicates are pseudo-compounds or mixtures of the two acid radicals. The general correspondence may be expressed by saying that where Clarke assumes the presence of Si_2O_6 (trisilicate) the suggested hypothesis assumes that of $(R'Si)_2$, and where he assumes SiO_4 (orthosilicate) this assumes $(R''Al)$. Clarke also, in common with Groth, Rammelsberg, Tschermak, and many others, considers the minerals under discussion as silicates, with the aluminum

* Bull. U. S. Geol. Surv., No. 125, 1895.

in the base, not as aluminosilicates, and Clarke furthermore regards them as substitution derivatives of aluminum silicates.

The present hypothesis differs from these views in that: (1), the acid radicals Si_2O_5 and SiO_2 are not regarded as mutually equivalent and isomorphously replaceable, as this is contrary to the accepted principles of isomorphism; (2), the feldspars, lenads, zeolites, and scapolites are regarded as salts of two aluminosilicic acids $\text{H}_2\text{AlSi}_2\text{O}_5$ for the first three and $\text{H}_2\text{AlSi}_2\text{O}_5$, for the last; (3), the hydrogens of these acids are assumed to be replaced, not by independent and variable atoms, but by atomic groups, here called "integrals," whose total valence is that of the basic hydrogens.

Attention must be called to the fact that, under the usual interpretation of the feldspars as silicates, the acids being $\text{H}_2\text{Si}_2\text{O}_5$ and $\text{H}_2\text{Si}_2\text{O}_5$, the groups $(\text{NaAl})^{\text{iv}}$ and $(\text{CaAl})^{\text{vi}}$ are essentially "integrals" exactly in the sense of those suggested in this paper.

Illustrations.—In the following pages will be given the constitutional formulas of the minerals under consideration, each group being followed by a brief discussion of some pertinent points. The names of the several integrals and appropriate names for the minerals, in accordance with a recently suggested mineral nomenclature,* have been coined, but are not given here, as introducing unnecessary complications. They will appear in a subsequent paper.

FELDSPAR GROUP.

ADULAR SUBGROUP, monoclinic or pseudomonoclinic.

Orthoclase, $(\text{KSi})\text{AlSi}_2\text{O}_5$	Soda-orthoclase, $\left\{ \begin{array}{l} m(\text{KSi})\text{AlSi}_2\text{O}_5 \\ n(\text{NaSi})\text{AlSi}_2\text{O}_5 \\ m(\text{KSi})\text{AlSi}_2\text{O}_5 \\ n(\text{BaAl})\text{AlSi}_2\text{O}_5 \end{array} \right\}$
Barbierite, $(\text{NaSi})\text{AlSi}_2\text{O}_5$	
Celsian, $(\text{BaAl})\text{AlSi}_2\text{O}_5$	
	Hyalophane, $\left\{ \begin{array}{l} m(\text{KSi})\text{AlSi}_2\text{O}_5 \\ n(\text{BaAl})\text{AlSi}_2\text{O}_5 \end{array} \right\}$

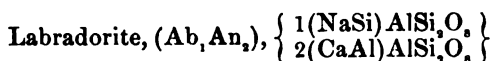
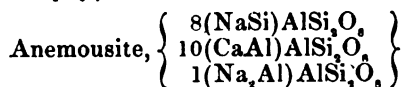
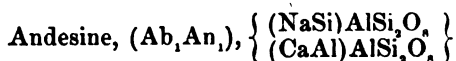
ALBITE SUBGROUP, triclinic.

Microcline, $(\text{KSi})\text{AlSi}_2\text{O}_5$	Anorthite, $(\text{CaAl})\text{AlSi}_2\text{O}_5$
Albite, $(\text{NaSi})\text{AlSi}_2\text{O}_5$	Carnegieite, $(\text{Na}_2\text{Al})\text{AlSi}_2\text{O}_5$
Calcium albite, $(\text{CaSi}_2)(\text{AlSi}_2\text{O}_5)_2$	

MIXED SALTS.

	Anorthoclase, $\left\{ \begin{array}{l} m(\text{KSi})\text{AlSi}_2\text{O}_5 \\ n(\text{NaSi})\text{AlSi}_2\text{O}_5 \end{array} \right\}$
Oligoclase, $(\text{Ab}, \text{An}_1)_2$	$\left\{ \begin{array}{l} 2(\text{NaSi})\text{AlSi}_2\text{O}_5 \\ 1(\text{CaAl})\text{AlSi}_2\text{O}_5 \end{array} \right\}$
	Sigterite, $\left\{ \begin{array}{l} 4(\text{KSi})\text{AlSi}_2\text{O}_5 \\ 2(\text{NaSi})\text{AlSi}_2\text{O}_5 \\ 9(\text{Na}_2\text{Al})\text{AlSi}_2\text{O}_5 \end{array} \right\}$

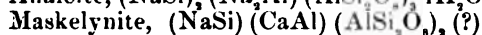
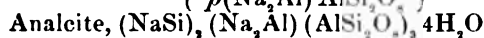
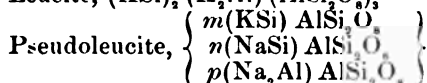
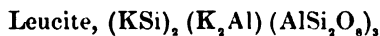
* H. S. Washington, this Journal, vol. xxxiii, p. 187, 1912.



In view of what has been said, it seems needless to point out that all these feldspathic salts are of identical chemical type, and are hence readily capable of isomorphous serial mixture, as is typically seen in the plagioclases and hyalophanes. The fact that they can all be referred to an orthosilicate formula, if aluminum is regarded as purely basic, has been referred to above. This, however, would seem to be a forced interpretation, and it is best to regard them all as salts of a (feldspathic) acid, $\text{H}_2\text{AlSi}_2\text{O}_6$, whose salts are polymorphous. As real monoclinic symmetry of orthoclase would necessitate, on this interpretation, that fellenadic acid be tetramorphous, it simplifies the problem, and is in accord with recent views, to consider it pseudomonoclinic. The salts of the general fellenadic acid are thus considered trimorphous, represented by triclinic anorthite, hexagonal nephelite, and isometric leucite.

The behavior of the feldspars with regard to acids is characteristic and significant. Orthoclase, microcline, albite, and barbierite, with only the silicic integral ($\text{R}'\text{Si}$) present, are unattacked, while anorthite and carnegieite (?), with ($\text{R}''\text{Al}$) present, are readily attacked, the former with production of gelatinous silica. Anorthoclase and the sodi-calcic feldspars follow the same rule, their resistance to acids increasing with the content in molecules containing the ($\text{R}'\text{Si}$) integral. Celsian and hyalophane, with the (BaAl) integral are only slightly attacked or unattacked by acids, but the barium salts are uniformly less soluble than the corresponding calcium ones.

LEUCITE GROUP, isometric or pseudo-isometric.



The formula for leucite, as thus expressed, shows an isomorphous mixture in stoichiometric proportions of fellenadates of two (KSi) molecules and one of (K_2Al). This complexity is in accord with its great instability and rarity in rocks, and

shows clearly its relation to pseudo-leucite. Analcite* has exactly the same form of molecule, but is a hydrated sodium leucite. On this interpretation both leucite and analcite are to be regarded as molecular compounds rather than mixed crystals or solid solutions, as is the case apparently with the originally isometric, but unstable, pseudo-leucite. In this connection attention may again be called to the isometric form of the $K_2Al_2Si_2O_8$ molecule observed by Lemberg and mentioned by Weyberg.†

The composition of maskelynite, a mineral only found in meteorites, is somewhat uncertain. The formula as given above agrees fairly well with the analysis, which was made on a small amount of unsatisfactory material.

	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	K ₂ O
Found	53.6	25.7	11.6	5.1	1.3
Calc.	55.6	28.2	10.4	5.8	

The formula $(NaSi)_2(CaAl)(AlSi_2O_8)_2$, which corresponds to that of leucite above, leads to the composition: $SiO_2 = 59.9$, $Al_2O_3 = 25.4$, $CaO = 7.0$, $Na_2O = 7.6$. It is possible that this is the true composition of the mineral, which needs reexamination, and that the figures found in the analysis, with lower silica and soda and higher lime, are attributable to admixed anorthite or labradorite.

It must be noted that all the minerals of the leucite group, in which the radical (R', Al) is prominent, are easily decomposed by acids, leucite without and analcite with gelatinization.

It may be added that, from their study of the action of ammonium chloride, Clarke and Steiger‡ conclude that: "analcite and leucite are not true metasilicates, but pseudo-compounds, either salts of a polymer of metasilicic acid, or mixtures of ortho- and tri-silicates analogous to those which we find among the plagioclase feldspars." Tschermak§ also considers that leucite is not a true metasilicate, but a salt of a polymeric acid, $H_2Si_2O_7$, which he calls "leucitic acid."

NEPHELITE GROUP, hexagonal.

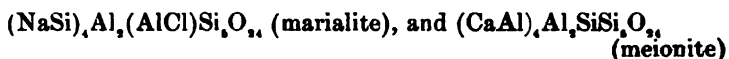
Nephelite, (artif.), $(Na, Al) AlSi_2O_6$, { $2(KSi)AlSi_2O_6$,
 Kaliophilite, $(K, Al) AlSi_2O_6$, Nephelite (5:1) { $10(Na, Al)AlSi_2O_6$,
 Eucriptite, $(Li, Al) AlSi_2O_6$, { $1(K, Al)AlSi_2O_6$,
 Cancrinite, $(Na, Al)_2(CaAl)[(NaCO_3)Al](AlSi_2O_6)_3 \cdot 3H_2O$

* The formula suggested here is in accord with the observation of Clarke and Steiger (Bull. U. S. G. S., No. 207, 1902, p. 9), that one-half of the Na of analcite is removed by heating in an open crucible with NH_4Cl . Unfortunately no data are given as to the same experiment with leucite.

† Weyberg, loc. cit. supra.

‡ Clarke and Steiger, Bull. U. S. Geol. Surv., No. 207, 1902, p. 19.

§ Tschermak, Zeitschr. Phys. Chem., 1905, p. 364.



It will be seen that this formula for marialite somewhat resembles that of sodalite as proposed by Brögger and Bäckström, $\text{Na}_4(\text{AlCl})\text{Al}_4\text{Si}_4\text{O}_{24}$.

It must be pointed out, however, that few of the analyses of the scapolites are satisfactory. This is partly because of the apparently great variability in composition, even at the same locality, partly because of defects obvious in the analyzes themselves, and partly because of the unsatisfactory character of the material, as the scapolites are very prone to alteration and the purity and freshness of the mineral analyzed is often not assured. A thorough, modern study of scapolites is highly desirable, carried out on carefully selected material of undoubted homogeneity, purity, and freshness, and by modern analytical methods.

As regards the action of acids, we see in this series the same relative resistance to attack induced by the presence of the integrals (NaSi) and (CaAl) as was found to be the case with the feldspars. According to both Dana and Hintze, marialite and mizzonite are only slightly or not at all attacked by HCl , wernerite is imperfectly decomposed, and meionite is wholly decomposed but without gelatinization.

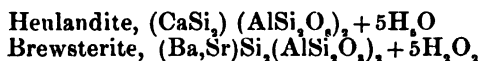
ZEOLITE GROUP, polymorphous.

The obviously very close relationship between the feldspars and lenads and the zeolites can be explained, and the whole group of "normal" zeolites (except apophyllite, mordenite, and ptilolite), can be harmonized, if we regard them as hydrated or sometimes acid or basic salts of the general fellenadic acid $(\text{H}_4\text{AlSi}_4\text{O}_{24})_n$, in which the integrals $(\text{R}'\text{Si})$ and $(\text{R}'\text{Al})$ replace the H_4 , and of which the feldspars and lenads are regarded as anhydrous salts. With the exceptions noted, all the well-defined zeolites proper can be reduced to this type of formula. The polymorphism of the anhydrous salts of fellenadic acid, taken in connection with the different degrees of hydration (since the different hydrates of a given salt show different crystal forms), logically explains the great diversity in crystal form of the zeolites, and the similarity in chemical constitution suggested here gives a reason for the crystallographic similarities of the two large groups of anhydrous and hydrated salts.

The function of water in the zeolites is as yet uncertain, although it has been the subject of much research and an extensive literature, which cannot be cited adequately here.

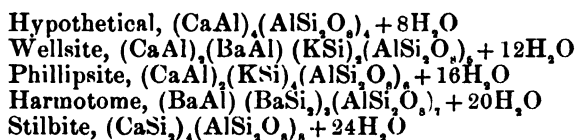
In most cases it is undoubtedly "water of crystallization" or but loosely attached to the crystal molecule, as is shown by its replaceability by NH_3 , H_2S , CS_2 , $\text{C}_2\text{H}_5\text{O}$, etc. But in other cases it certainly, or almost certainly, exists, at least in part, as acidic hydrogen or basic hydroxyl. In view of this uncertainty all the zeolitic water is regarded in the following formulas as "of crystallization," but were it constitutional, in part or entirely, it could be introduced in the molecular formulas without change of type and with only slight increase in complexity. The chemical compositions of all the zeolite formulas here given have been calculated and found to agree with the results of analysis. It will be noted that the introduction of the decivalent radical $(\text{CaSi}_3)_n$, which would be present in a calcium albite, is necessary in some cases.

HEULANDITE SUBGROUP, monoclinic.



Heulandite is obviously the pentahydrate of calcium albite and brewsterite the pentahydrate of a corresponding barium-strontium salt.

PHILLIPSITE SERIES, monoclinic.



These minerals apparently represent a homologous series, as was pointed out by Fresenius, cited by Pratt and Foote.* It would seem that considerable isomorphous replacement is possible among the integrals, and several parallel pure series might exist. The authors cited suggest a hydrated calcium anorthite and a hydrated calcium albite as the end members. The first of these is shown above, though as yet unknown, and the latter would have the composition of stilbite. The formulas are given in the form above so as to bring out the serial relationship, but several of them can be simplified by division. Thus reduced to their simplest terms, the hypothetical end member would be an anorthite di-hydrate and stilbite a calcium albite hexa-hydrate.

* Pratt and Foote, this Journal, iii, p. 448, 1897.

CHABAZITE SUBGROUP, trigonal.

Gmelinite, $(\text{NaSi})_2(\text{Na}, \text{Al})(\text{AlSi}_2\text{O}_6)_2 + 12\text{H}_2\text{O}$ Chabazite, $(\text{NaSi})_2(\text{CaAl})(\text{AlSi}_2\text{O}_6)_2 + 12\text{H}_2\text{O}$ Levynite, $(\text{CaSi})_2(\text{CaAl})(\text{AlSi}_2\text{O}_6)_2 + 12\text{H}_2\text{O}$

Gmelinite is here regarded as the purely sodic, and levynite as the purely calcic, member of an isomorphous series like that of the feldspars and scapolites. The commonly occurring intermediate chabazites are mixed crystals of variable composition, and the one chosen for illustration is that midway between the extremes. The ratios here given are exactly stoichiometric, but not necessarily found in nature, though the tendency would be to approximate to such ratios, as is also the case with the sodi-calcic feldspars. It will be remarked that the formula of gmelinite is that of a dodeca-hydrate of sodium leucite and that of levynite of a similar hydrate of calcium leucite.

Similarly, analcite is the tetrahydrate of sodium leucite.

NATROLITE SUBGROUP, orthorhombic and monoclinic.

Natrolite, $(\text{NaSi})_2(\text{Na}, \text{Al})(\text{AlSi}_2\text{O}_6)_2 + 8\text{H}_2\text{O}$ Scolecite, $(\text{CaSi})_2(\text{CaAl})(\text{AlSi}_2\text{O}_6)_2 + 12\text{H}_2\text{O}$ Mesolite, $(\text{NaSi})_m(\text{CaAl})_n(\text{AlSi}_2\text{O}_6)_{m+n} + p\text{H}_2\text{O}$

Owing to the difference in crystal form and in water content there is some doubt as to whether these minerals form a group or series in the sense here suggested, but it is probable that such is the case. It is interesting to note that the formula of natrolite corresponds exactly, apart from the water, with that of Rammelsberg's sigterite given above, while that of a mesolite, with $\text{Na}_2\text{O} : \text{CaO} = 1 : 2$, and also minus the water, is that of the anemousite of Linosa, as has been previously pointed out.*

UNGROUPED ZEOLITES.

Laumontite, $(\text{CaSi})_2(\text{CaAl})(\text{AlSi}_2\text{O}_6)_2 + 12\text{H}_2\text{O}$ Analcite, $(\text{NaSi})_2(\text{Na}, \text{Al})(\text{AlSi}_2\text{O}_6)_2 + 4\text{H}_2\text{O}$ Faujasite, $(\text{NaSi})_2(\text{CaSi})_2(\text{CaAl})(\text{AlSi}_2\text{O}_6)_2 + 40\text{H}_2\text{O}$ Edingtonite, $(\text{BaSi}_2)(\text{BaAl})(\text{AlSi}_2\text{O}_6)_2 + 12\text{H}_2\text{O}$ Thomsonite, $(\text{Na}, \text{Ca})(\text{Al})(\text{AlSi}_2\text{O}_6)_2 + 5\text{H}_2\text{O}$ Hydronephelite, $(\text{Na}, \text{Al})(\text{HSi})(\text{AlSi}_2\text{O}_6)_2 + 3\text{H}_2\text{O}$

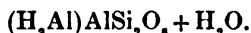
As regards the action of acids the zeolites, being hydrated salts and of somewhat "loose" structure, as shown by the behavior of their water content, are naturally more readily attacked than the anhydrous minerals discussed previously.

* Washington and Wright, this Journal, xxix, p. 57, 1910.

From a survey of the literature it appears that, while they are all attacked by hydrochloric acid, yet the tendency noted above is also manifest here. In general those which contain the greater proportions of the (R'Si) integrals are not apt to furnish gelatinous silica, while this is the common product with those which show much or most of (R''Al).

KAOLINITE, monoclinic.

As has been noted on a previous page, kaolinite is the most usual and most common end product of the alteration of the feldspars, lenads, scapolites, and zeolites. Its relation to them, and the reason for this fact, are readily seen if we write its formula as follows, assuming the presence of an (R',Al) integral, R' here being hydrogen :



This is simply a transformation of the usual formula, $H_2Al_2Si_2O_7$. On this basis kaolinite is to be considered as a hydrated acid aluminum salt of fellenadic acid, the univalent and bivalent metals having been carried off in solution. In the process of alteration the integrals (R'Si) would furnish the quartz generally found along with kaolin, while hydrogen replaces the metal atoms. The persistence of the (R'',Al) integral is in harmony with many observations on the weathering of rocks, in which it has been shown that the alumina is the component which undergoes the least loss, and which has, therefore, been used by Merrill and others as a standard of measurement of the alteration undergone.

Locust, N. J., March, 1912.

SCIENTIFIC INTELLIGENCE.

I. CHEMISTRY AND PHYSICS.

1. *The Preparation of Perchloric Acid*.—For this purpose H. H. WILLARD employs ammonium perchlorate, a comparatively inexpensive salt. He decomposes this by boiling its solution with *aqua regia*, evaporates off the excess of the latter and thus obtains the perchloric acid. The yield is theoretical, since the perchloric acid takes no part in the destruction of the ammonia. By the use of pure materials the acid may be thus obtained in a pure condition, but the author recommends the distillation of the acid at a pressure of about 100^{mm}, and gives details in regard to the apparatus. The acid obtained either by evaporation or by subsequent distillation corresponds nearly to the formula $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.

An interesting matter in connection with this work on the preparation of perchloric acid is the study which the author has made concerning the destruction of ammonia by *aqua regia*. He has found that chlorine gas alone when passed into the boiling solution has little effect, but that nitrous acid is the active agent, as was shown by the fact that nitric acid and a reducing agent, such as formic acid, would destroy the ammonium salt. The most unexpected result was the fact that the gas given off by the action of *aqua regia* upon an ammonium salt is chiefly nitrous oxide, N_2O . The prevailing opinion that nitrogen gas is the principal product under these circumstances must now be abandoned as erroneous.—*Jour. Amer. Chem. Soc.*, xxxiv, 1480.

H. L. W.

2. *Centenary Celebration of the First Commercial Gas Company*. Edited and Published by the American Gas Institute. 8vo, pp. 174. New York, 1912 (29 West 39th st., New York City).—This book contains the lectures delivered at the celebration, held in April, 1912, at the Franklin Institute in Philadelphia, of the centenary of the event of the first commercial sale of gas as an illuminant. An interesting chronology of the early development of gas lighting, as well as a description of a loan exhibition of historical objects relating to the industry is included. The lectures are on by-products of gas manufacture by Professor Charles E. Monroe, on the commercial aspects of the gas industry by Hon. George B. Cortelyou, on the technique of gas manufacture by Alfred E. Forstall, on gas as an illuminant by Van Rensselaer Lansingh, and on the use of gas for heat and power, and on the testing of gas by E. B. Rosa.

H. L. W.

3. *The Analyst's Laboratory Companion*; by ALFRED E. JOHNSON. 12mo, pp. 164, Philadelphia, 1912 (P. Blakiston's Son & Co.).—This American issue of a British book is a collec-

tion of tables and data for the use of public and general analysts, agricultural, brewers' and works' chemists and students. It gives also numerous examples of chemical calculations and concise descriptions of several analytical processes. The tables appear to be well selected for their purpose and carefully prepared, and the book will be useful to analytical chemists. Certain data relating to the imperial gallon, and statements in regard to British food regulations are not applicable in this country. A few tables give 7-place logarithms, which are much longer than is necessary for the data to which they are to be applied. The table of factors for gravimetric analysis is a good one, and here mantissas of only 5-places are employed. The 5-place logarithm table given in the book is not a very convenient one, since when used as an anti-logarithm table it usually gives only three figures without interpolation.

H. L. W.

4. *A College Text-Book on Quantitative Analysis*; by H. R. MOODY. 8vo, pp. 165. New York, 1912 (The Macmillan Company).—Very elaborate directions, explanations and notes are given here for a course of laboratory work. The operations included are mostly of the very simplest character, and their number is so small that the work seems hardly worthy of the designation of "College text book." The gravimetric part includes only the determinations of aluminium, copper, iron, chlorine and sulphuric acid in simple salts, of calcium and magnesium in dolomite, and of silica in a silicate. "Section II, Electrolytic Analysis," gives only the determinations of silver and copper. Under volumetric analysis are given the preparation and standardization of half-normal hydrochloric acid and sodium hydroxide, the determination of total alkali in soda ash, of chlorine with silver nitrate, and of iron with permanganate. With such a limited scope, it is hardly to be expected that the book will find wide use outside of the author's laboratory.

H. L. W.

5. *Per-acids and their Salts*; by T. SLATER PRICE. 8vo, pp. 123. London, 1912 (Longmans, Green and Co.).—This is one of a series of monographs on inorganic and physical chemistry edited by Professor Alexander Findlay. It gives a very satisfactory presentation of a branch of chemistry which has been very actively investigated in recent years, and it will be of great assistance to teachers and advanced students who desire a fuller and more modern presentation of the subject than is given in ordinary text-books. The topics dealt with are, persulphates and perselenates, perborates, percarbonates, pernitric and perphosphoric acids, pertitanates, perzirconates and perstannates, pervanadates, percolumbates and pertantalates, perchromates, permolybdates, pertungstates and peruranates. There is also a very full list of references to the literature.

H. L. W.

6. *Lehrbuch der Chemischen Technologie und Metallurgie*; herausgegeben von Dr. BERNHARD NEUMANN. 8vo, pp. 891, Leipzig, 1912 (Verlag von S. Hirzel).—This text-book for students has been prepared by the collaboration of eminent specialists

in the various subjects. Consequently the topics are treated from an entirely modern point of view. The articles are concise and clear, and treat the subjects very satisfactorily for the use of students. Usually some important historical points are given, as well as some important statistics, but the articles are devoted chiefly to clear descriptions of the processes and the principles involved in them. The work is a very valuable one, and furnishes the most useful information to those who are interested in the development of applied chemistry and metallurgy.

H. L. W.

7. *Räumliche Intensitätsverteilung der X-Strahlen, die von einer Platinantikathode ausgehen.*—The question of the distribution of intensity of Röntgen rays has once more come to the front as a consequence of the experimental demonstration, by Barkla and others, of the polarization of these rays. According to the pulse theory of X-rays the intensity should be greater at right angles to the direction of the exciting cathode rays than in a direction parallel to the latter; also, the hardness should increase with decreasing azimuth. The term "azimuth" is here used to designate the angle which the axis of the cathode-ray beam makes with the axis of the associated X-ray pencil. This problem has been successfully attacked by W. FRIEDRICH, who used both photographic and electric methods of experimentation.

The uncertainty arising from the inevitable variations in the thickness of the glass walls of the focus tube was minimized by affixing a little glass plate to the outside of the X-ray bulb at each of the fourteen azimuths at which the intensities of the rays were studied. These laminæ were of such thickness as to compensate for the inequalities of the walls of the Röntgen ray bulb. Other investigators have attempted to eliminate this source of error by theoretical calculations. For obvious reasons the author used a platinum anticathode. In the photographic method the X-ray pencils were separated from one another by suitable lead screens so placed around the bulb as to allow only narrow wedges of rays to fall upon the sensitized surface. In this way a series of parallel "lines," corresponding to the various azimuths, were registered by the cylindrically folded photographic film. This method possessed the great advantage of recording all of the impressions simultaneously. The advantage thus gained was offset, however, by our present ignorance of the law of photographic blackening produced by Röntgen rays. In the electrical method two condensers of special construction were employed. One condenser was kept fixed at a chosen standard azimuth, while the other condenser was set successively at each of the remaining azimuths. The advantage of simultaneity was lost, but the errors arising from this cause were minimized by repeating the observations a large number of times. On the other hand, the ionization currents set up by the passage of the X-rays through the gas in the condensers could be easily measured, so that definite quantitative results were obtained. In general, the photographic

process verified the electrical method and, when this was not the case, the author gives a valid explanation of the divergence, the photographic method being subject to secondary influences which were eliminated in the electrical experiments.

In substance, Friedrich summarizes his results as follows:

1. The intensity of X-rays, which come from a platinum anticathode and which pass through a uniform thickness of 2^{mm} of compensated glass wall, shows a dependence upon the azimuth, when investigated either by the photographic or by the electric method.
2. The maximum of intensity does not lie at right angles to the direction of the cathode ray beam, but is displaced towards the side of the azimuths less than 90° . The harder the X-rays, the greater is this displacement.
3. The determination of the distribution of intensity by the electrical method gives, on the average, a difference of intensity of 20 per cent between the azimuths 80° and 150° .
4. The hardness of the X-rays is likewise a function of the azimuth. It increases, for the directions studied, with decreasing azimuth.
5. At the azimuth 0° a minimum of intensity of X-rays which had come from a platinum anticathode and which had passed through a sheet of aluminium 0.01^{mm} thick, was established photographically.—*Ann. d. Phys.*, No. 12, September, 1912, p. 377.

H. S. U.

8. *Experimentelle Bestimmung des Verhältnisses der spezifischen Wärmen c_p/c_v bei Kalium- und Natriumdämpfen und daraus sich ergebende Schlussfolgerungen.*—As is well known, lithium, potassium, and sodium obey the law of Dulong and Petit. Furthermore, vapor density determinations have led to the conclusion that the vapors of cadmium, lead, mercury, silver, thallium, and zinc are monatomic. These, and other facts, have led F. Richarz to advance the hypothesis that, in general, metallic vapors consist of monatomic molecules. By improving the apparatus used by his predecessors, MAX ROBITZSCH has verified this hypothesis for the vapors of potassium and sodium.

A steel tube about 70^{cm} long and 2.8^{cm} internal diameter was placed inside an electric furnace. This tube was provided with a steel piston which enabled the experimenter to vary at will the length of the column of vapor inside the tube. The other end of the tube was closed by a thin membrane of mica. The chief improvement in the apparatus consisted in placing an adjustable resonance tube between the mica membrane and the exciting pitch pipe. When both the resonator and the pitch pipe were carefully tuned to one of the natural periods of vibration of the membrane, very definite maxima of sound intensity could be observed when the steel piston occupied the proper positions one-half of a wave-length apart. The steel tube was filled with the indifferent gas nitrogen before the introduction of the metal to be vaporized.

For potassium vapor having a temperature between 950°C . and 1000°C . the ratio γ of the specific heat at constant pressure to that at constant volume was found experimentally to be 1.64. From

880°–920°, $\gamma = 1.69$; from 700°–730°, $\gamma = 1.63$; and from 680°–700°, $\gamma = 1.61$. Similar results were obtained with sodium vapor. Since, within the limits of experimental accuracy, the ratio of the specific heats for potassium and sodium vapors remains constant from high temperatures down to the immediate neighborhood of the boiling point, and since this ratio has approximately the value 1.667, which is required by theory for monatomic gases, the author concludes that no polymerization takes place even down to the point of liquefaction itself. This result is in complete accord with the investigations of Richarz which led to the conclusion that monatomicity prevails for the alkali metals in the solid state. From all of his experimental data Robitzsch calculates the following probable mean values for the vapors of potassium and sodium respectively: $\gamma = 1.64 \pm 0.007$ and $\gamma = 1.68 \pm 0.03$. The corresponding values of the ratio of the speed of sound in the metallic vapors to the speed of sound in air are given as 0.933 ± 0.002 , and 1.233 ± 0.006 , in the order named.—*Ann. d. Phys.*, No. 10, August, 1912, p. 1027. H. S. U.

9. *Untersuchungen über magnetische Zerlegung feiner Spektrallinien im Vakuumlichtbogen.*—The Zeeman effect exhibited by certain fine lines of bismuth, cadmium, thallium, and zinc has been recently investigated by CH. WALI-MOHAMMAD. For this purpose he used a modified form of Janicki lamp and an excellent echelon spectroscope. The results obtained are too numerous to admit of a detailed account in this place, nevertheless the general conclusions deserve quotation.

It was found that the Janicki type of oxide cathode lamp gave very fine, intense satellites so that it affords an excellent source for studying the Zeeman effect. A few satellites were investigated for the first time. Some of the satellites were resolved by the magnetic field into three, four, five, six, and even nine components. In general, the separation was proportional to the magnetic field strength. One companion line of cadmium $\lambda = 4800$ gave an extraordinary type of resolution. Another satellite of this principal line showed that the law of displacement changed as the intensity of field was increased. The cadmium line $\lambda = 4678$ has satellites which are visible in the magnetic field but which cannot be seen under ordinary conditions. The bismuth line $\lambda = 4722$ has a very complicated structure, and two of its satellites suffer a magnetic displacement which is proportional to the square of the field strength. Finally, the author found that the resolution of sufficiently fine lines could be measured in very weak fields, such as 300 gauss.—*Ann. d. Phys.*, No. 11, September, 1912, p. 225. H. S. U.

10. *The Absorption Spectrum of Tellurium Vapor and the Effect of High Temperature upon it.*—The dependence of the absorption spectrum of tellurium vapor upon temperature has been investigated for the first time by E. J. EVANS. The vapor in question was heated in a quartz tube placed inside an electric furnace, the temperature of which was determined by the aid of

a Pt-Pt-Rh thermocouple. The quartz tube was provided with a lateral tube of 3^{mm} or 4^{mm} bore in which the solid tellurium was placed, and after this apparatus had been evacuated to a pressure of 0.1^{mm} or less, the side tube was sealed off in an oxyhydrogen flame. The pressure of the vapor was varied by sending currents of different strengths through a nickel wire wound around the side tube. The temperature of the coolest part of this tube was determined, since the pressure inside the main tube depended upon it. After the furnace and lateral tube had been regulated to their respective temperatures, the light from the positive pole of a carbon arc was passed through the vapor and focussed on the slit of a small concave grating spectrograph. The absorption spectrum was examined for the interval λ 2400 to λ 7000, and for temperatures varying between about 500° C. and 1350° C. In one series of experiments the pressure was kept constant and the temperature varied, while in another series a known mass of tellurium was placed in a quartz tube and the absorption spectrum photographed at different temperatures.

The results of this investigation are summarized by the author in the following words: "1. The bands in the absorption spectrum of tellurium extend from λ 3900 to about λ 6000. In addition to a band spectrum the vapor gives a general selective absorption. The absorption spectrum of tellurium is similar to that of selenium, but compared with the spectrum of the latter is displaced toward the red. 2. For small pressures absorption bands are first photographed in the extreme violet (λ 3900), and as the pressure increases, absorption bands are also photographed in regions of greater wave-length. At pressures sufficient to show the presence of bands in the region λ 5300— λ 6000, there is complete absorption in the violet and blue. 3. When the pressure of the vapor is low, the absorption bands in the region λ 3900— λ 4500 diminish in intensity with increase of temperature until they almost disappear at 1200° C. This result may be explained on the hypothesis that the absorption bands are due to complex molecules, which are present in tellurium vapor at low temperatures. These molecules are completely dissociated at high temperatures and hence the absorption bands are not visible. 4. The absorption spectra of a constant mass (0.002 gm.) of tellurium vapor at 1000° C. and 1350° C. do not show any difference. Both spectra show the presence of bands between λ 5300 and λ 6000 and a continuous absorption from λ 5300 to λ 3500. The intensities of the bands are not affected by a change of temperature from 1000° C. to 1350° C. From the experimental results it is impossible to determine whether these bands are due to diatomic molecules or more complex ones."—*Astrophys. Jour.*, vol. xxxvi, October, 1912, p. 228.

H. S. U.

II. GEOLOGY.

1. *New York Potsdam-Hoyt Fauna and Group Terms for the Lower and Upper Cambrian Series of Formations*; by CHARLES D. WALCOTT. Smithsonian Misc. Coll., Vol. 57, Nos. 9 and 10, pp. 251-307, pls. 37-49, 1912.—The first paper is in the main a description of the Potsdam and Hoyt faunules, the former having 19 species (4 new) and the latter 10 (1 new). *Lingulepis acuminata* is the only species common to both assemblages. A new genus of gastropod, *Matherella*, is described. The striking new illustrations are as follows: (1) Climactichnites, a track that may have been made by a mollusk (Woodward) but which Walcott thinks is the trail of a large annelid; (2) tracks of Protichnites that "were made by trilobites of the genus *Dicellosephalus*" (278); and (3) the four fine figures of the Middle Cambrian trilobite *Neolenus serratus*, showing remarkably long and stout walking legs with three terminal spines that are also thought to have been present in *Dicellosephalus* (Protichnites track).

Walcott still regards the Potsdam-Hoyt formations as belonging "to the upper limit of the Cambrian" (p. 255) and dissents from Ulrich's view that they belong higher in the geologic scale. They are equivalent, he states, "with the fauna of one of the upper horizons of the 'St. Croix sandstone' and thus included in the Upper Cambrian" (p. 255).

Due to the principle of priority of definition and the limitation of a stratigraphic term to one meaning, Walcott in No. 10 substitutes *Waucoban* (from Waucoba, California) for the series (or Lower Cambrian) term *Georgia*. The latter is, therefore, to be retained as originally proposed for the slates of Georgia, Vermont. For similar reasons Walcott's series term *Saratogan* cannot be retained as it is based upon the Saratoga formation of New York, and further the name is preoccupied by Branner for a Cretaceous deposit of Arkansas. Walcott now proposes that we use *St. Croixan*, based upon N. H. Winchell's "St. Croix beds" named by him in 1873. In 1902 (p. 636) Ulrich and Schuchert called this late Middle and Upper Cambrian sea invasion the "St. Croix invasion" and Ulrich in 1911 also used as a stratigraphic term "St. Croixan," the equivalent for his Upper Cambrian. Under these circumstances the term *St. Croix* has now three meanings and according to modern geologic usage can be retained only in one sense, namely, that of the first user. As subsequent workers have given names to the different members of the *St. Croix* beds and as Winchell used the term for all the Cambrian deposits of the upper Mississippi region, his term could by general consent be used in the sense proposed by Ulrich and Walcott, but according to strict usage and the rules employed by the U. S. Geological Survey, it seems to the reviewer that it cannot now be used in this wider and double sense. The proposer of a new substitute will have to bear in mind the systemic term "Ozarkian" of Ulrich, and the complications are, therefore, many. c. s.

2. *Volcanic vortex rings and the direct conversion of lava into ash*; by FRANK A. PERRET.—In the article upon the above subject in the November number, figure 3 on p. 408 has unfortunately been printed upside down.

III. MISCELLANEOUS SCIENTIFIC INTELLIGENCE.

1. *National Academy of Sciences*.—The regular autumn meeting of the National Academy was held in New Haven on November 12, 13. President Remsen occupied the chair and upwards of forty-five members were in attendance; the sessions were held in the new Sloane Physical Laboratory. The following is a list of the papers presented:

CHARLES D. WALCOTT: Cambrian formations of Mount Robson District, British Columbia.

WILLIAM M. DAVIS: Physiographic evidence in favor of the subsidence theory of coral reefs.

WILLIAM B. SCOTT: Restorations of Tertiary mammals.

HENRY F. OSBORN: Geologic correlation of upper Palaeolithic Faunas of Europe and America.

JOHN M. CLARKE: The Devonian faunas of Western Argentina. Probable Devonian glacial boulder beds in Argentina.

CHARLES SCHUCHERT: Climates of geologic time.

WILLIAM M. DAVIS: The transcontinental excursion of the American Geographical Society.

ARNOLD HAGUE: Biographical memoir of Samuel Franklin Emmons.

JACQUES LOEB: On the fertilization of the egg of invertebrates with blood.

EDWIN G. CONKLIN: Cell division and differentiation.

CHARLES B. DAVENPORT: Heredity of skin color in negro-white crosses.

LAFAYETTE B. MENDEL: Some bio-chemical features of growth.

THOMAS B. OSBORNE: The nutritive value of the proteins of maize.

ROSS G. HARRISON: Experiments of regeneration and transplantation of limbs in the Amphibia.

S. J. MEUTZER: Theory and fact as illustrated by an instructive experiment on the splanchnic nerve.

FRANZ BOAS: New data on the influence of heredity and environment upon the bodily form of man.

ERNEST W. BROWN: The problem of the asteroids.

ROBERT W. WOOD: Some results obtained with the most powerful spectrograph in the world. On the possibility of photographing molecules. On a new method of finding regularities in band spectra.

CHARLES C. ADAMS: The variations and ecological distribution of the snails of genus *Io*.

At the coming spring meeting, to be held at Washington in April, 1913, the semi-centennial of the Academy will be commemorated.

OBITUARY.

Professor JOHN WILLIAM MALLET, the eminent chemist of the University of Virginia, died on November 6 at the age of eighty years. He was born in Dublin, Ireland, and received his B.A. degree from Trinity College in 1853. His life was chiefly spent in this country, where he held several important positions; he was a member of numerous scientific societies, and made many original contributions to general and applied chemistry.

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